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ADVANCED THERMOPLASTIC COMPOSITE DEVELOPMENT.(U)  
MAY 79 S G HILL, E E HOUSE, J T HOGGATT

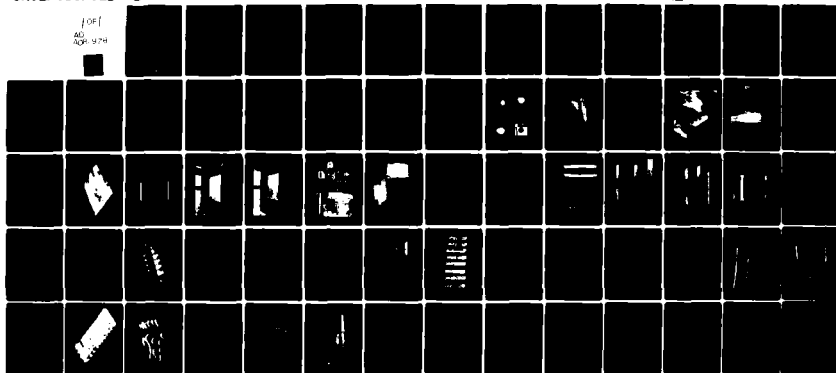
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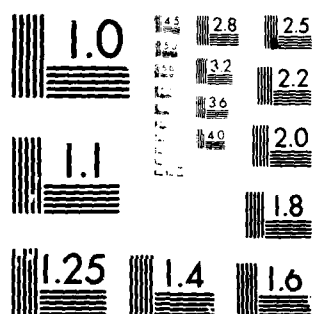
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FINAL REPORT  
ADVANCED THERMOPLASTIC COMPOSITE DEVELOPMENT  
CONTRACT N00019-77-C-0561

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By

S. G. Hill  
E. E. House  
J. T. Hoggatt

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Prepared for

NAVAL AIR SYSTEMS COMMAND  
U.S. DEPARTMENT OF THE NAVY  
Washington, D.C. 20360

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MAR 12 1980

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May 1979

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Boeing Military Airplane Development Organization  
Boeing Aerospace Company  
Seattle, Washington 98124

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## FOREWORD

This report summarizes the work performed by the Boeing Aerospace Company during the period from November 4, 1977 to February 4, 1979 for the Naval Air Systems Command, United States Department of the Navy, under Contract N00019-77-C-0561 entitled, "Advanced Thermoplastic Composite Development." Mr. Maxwell Stander (AIR 5163D3) was the program manager.

The program was conducted by the Boeing Military Airplane Development organization of the Boeing Aerospace Company, Seattle, Washington. Mr. J. T. Hoggatt was program manager; Mr. E. E. House and Mr. S. G. Hill were principal investigators.

Key personnel contributing to the program were Mr. R. Hodges, Ms. V. Monroe, and Ms. J. Jaquish.

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## 1.0 INTRODUCTION AND SUMMARY

During the past 10 years, the capability of graphite-reinforced epoxy matrix composites to save weight in selected aircraft applications has been satisfactorily demonstrated on programs funded by various DOD agencies and commercial aircraft manufacturers. At present, high cost and limited in-service performance data are major factors that curtail the use of these high-performance materials. The need for in-service data will be resolved by the recent commitment to use graphite/epoxy composite structures on new military and commercial aircraft models. However, the ability to produce graphite/epoxy structure that is cost-competitive with conventional metallic construction is rarely achieved except in carefully selected applications where a significant reduction in part count occurs or where expensive machining operations are eliminated. Since graphite/epoxy material is more expensive than the metal, aluminum, that it will replace, the cost of fabricating composites must be made significantly lower than for metals to compensate for the difference in price of the two materials. This is difficult to achieve for several reasons: composite construction is labor-intensive, especially when hand layup techniques are used; automated layup equipment is expensive and custom made, and its reliability is not thoroughly proven; refrigerated storage and special handling procedures of prepreg are required; and stringent (costly) receiving, storage, and in-process quality control procedures are required.

One potential solution to the cost problem is the use of thermoplastic matrix composites. While the cost of thermoplastic matrix prepreg is comparable to that of epoxy prepreg, thermoplastics are better suited to high-speed, low-cost fabrication processes and are expected to produce significant cost reductions in that area. Other cost-reduction attributes of thermoplastic matrix composites include: refrigerated storage is not required; the composites can be postformed; simple joining processes such as welding and fusion can be used; special handling, transportation, and cleaning procedures are not required; there is reduced scrappage; out-of-contour parts can be reprocessed; and design modifications and repairs requiring localized doublers and/or check-and-straighten operations are easily accomplished. In addition to thermoplastic matrix composites possessing many of the desirable storage and processing characteristics of metals, thermoplastics do not corrode or require heat treatment after forming, nor does welding reduce the mechanical properties of the thermoplastic composites. These factors provide a degree of flexibility in design, fabrication, and repair operations not possible with other materials.

The structural adequacy of polysulfone thermoplastic matrix composites has been demonstrated on previous contracts (ref. 1-4). However, it is desired that the thermoplastic matrix have better resistance than polysulfone to fluids encountered in aircraft flight and maintenance operations.

Recognizing the foregoing situation, the objectives of the program were (1) to evaluate graphite-reinforced thermoplastic composites that show promise of improvement in environmental resistance over graphite/P1700 polysulfone composites; (2) to evaluate environmental resistance, forming limitations, and stability to thermal cycling of metal clad graphite/thermoplastic composites; and (3) to investigate repair procedures using thermoplastic materials. These objectives were accomplished during this program, which was conducted in three separate tasks: Task I—Resin and Composite Characterization, Task II—Metal Clad Composites, and Task III—Repair Evaluation. A brief summary of each task follows:

#### TASK I—RESIN AND COMPOSITE CHARACTERIZATION

During this task, resins were selected, characterized, and then impregnated onto graphite reinforcement. The resulting prepregs were molded into laminates and evaluated for physical, mechanical, and fluid resistance properties. The resins studied were Union Carbide Radel 5010 polyphenylsulfone, PKXA .41 and .517 silane end-capped polysulfones, and ICI 300P polyethersulfone. Limited evaluations also were performed on a fluorocarbon-based resin from Allied Chemical designated CM-1 and a polyethersulfone (KM-1) supplied by ICI. Laminates prepared from graphite fabric/Radel 5010 prepreg exhibited mechanical properties comparable to those of graphite fabric/P1700\* polysulfone, which was the standard against which all laminate properties in this task were measured. However, the solvent resistance of the Radel 5010 laminates was not to the desired level as determined by stressed and unstressed flexure specimens immersed in fluids commonly used in aircraft flight and maintenance operations. Mechanical properties and fluid resistance of the PKXA .41 and .517 laminates were lower than anticipated and this was attributed to aging (cross-linking) of the resin prior to impregnation. The 300P laminate exhibited acceptable physical and mechanical properties, but the fluid resistance was not at the desired level. The

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\*Union Carbide "Udel"

CM-1 and KM-1 resins were received too late in the program to be adequately characterized. However, graphite/CM-1 laminates were not affected when immersed in fluids known to degrade other thermoplastic matrix composites, and both the CM-1 and KM-1 laminates possessed promising mechanical properties.

#### TASK II—METAL CLAD COMPOSITES

In Task II, graphite fabric reinforced Radel 5010 and 300P laminates were clad with 0.010-inch titanium to further enhance their fluid resistance. Specimens were subjected to stressed and unstressed exposure in selected fluids, postforming studies, and thermal cycling. The metal cladding did not improve the fluid resistance of the composites. In the postforming studies, it was determined that the parts could be postformed without delaminating the metal cladding from the composite laminate. Thermal cycling had no detrimental effect on the metal clad composites.

#### TASK III—REPAIR EVALUATION

During this task, quick, easy-to-perform repair procedures using thermoplastic materials were explored. Two of these procedures, spot fusion and the use of a glue-gun, were demonstrated to the extent needed to show that they are viable repair procedures.

## 2.0 TECHNICAL DISCUSSION

The objectives of this program were (1) to evaluate graphite-reinforced thermoplastic composites that show promise of improvement in environmental resistance over graphite/P1700 polysulfone composites; (2) to evaluate environmental resistance, forming limitations, and stability to thermal cycling of metal clad graphite/thermoplastic composites; and (3) to investigate repair procedures using thermoplastic materials. To accomplish these objectives, the program was divided into three principal areas: Task I—Resin and Composite Characterization, Task II—Metal Clad Composites, and Task III—Repair Evaluation.

### 2.1 TASK I—RESIN AND COMPOSITE CHARACTERIZATION

In Task I, resins were selected, characterized, impregnated onto the graphite reinforcement, and then molded into laminates for physical and mechanical properties determinations. Also, the effect of stressed and unstressed environmental exposure on the laminates was evaluated. The approach used to accomplish these efforts is presented in the Figure 1 flow diagram.

#### 2.1.1 Polymer and Reinforcement Selection

It was intended to evaluate four thermoplastic resins during Task I. At the onset of the program, there were three recently developed resins from Union Carbide Corporation available for evaluation. They were Radel 5010 polyphenylsulfone and two silane end-capped polysulfones designated PKXA .41 and PXKA .517. The PKXA .517 is a higher molecular weight polymer than PKXA .41. Radel 5010 resin was commercially available, while the PKXA resins were in a laboratory development stage with samples on hand from a previous contract (ref. 3). The fourth resin, ICI's polyethersulfone 300P, was selected from several promising candidates including bis-A-phenyl based polymers developed by Union Carbide. The bis-A-phenyl based polymers were not available for evaluation under this program and Union Carbide projected that the high polymer manufacturing costs might preclude the resins from becoming commercially available, at least in the immediate future.

Another class of thermoplastics, polyarylates, developed by Unitika, Ltd., Japan and marketed by Union Carbide Corporation under the trade name of Ardel," was

Select Polymers and Reinforcement



Characterize Polymers



Process Development



Mechanical Properties



Environmental Exposure



Select Composites for Task II

Figure 1. Task I Flow Diagram

considered but rejected as a suitable candidate for composite applications. According to Union Carbide, Ardel resins are soluble in methylene chloride and no improvement in fluid resistance over P1700 polysulfone is projected.

The selection of 300P was based upon evaluation of a similar polyethersulfone, 200P, under a previous contract (ref. 2) in which graphite/200P was shown to be a promising laminate material combination, but fluid resistance was not studied.

A limited evaluation performed under the reference 3 contract had shown graphite/PKXA laminates to be resistant to solvents, such as methylene chloride, that readily dissolve polysulfone resin. This resistance to solvent attack was postulated to be due to crosslinking of the PKXA polymer during the molding cycle or possibly some type of chemical reaction between the resin and graphite and/or fiber surface finish. Regardless of what was imparting solvent resistance to the PKXA laminates, they were considered primary candidates for further study. Since postforming capabilities would be affected by the degree of crosslinking (if any) taking place, forming studies on PKXA laminates during this program were felt to be in order.

As the program progressed, two additional resins, reported by their suppliers as being resistant to aircraft fluids, were made available to the program. They were polyethersulfone from ICI designated KM-1, and CM-1 fluorocarbon based resin from Allied Chemicals. These materials were received near the end of the program with sufficient time available for only a preliminary evaluation.

The reinforcement used exclusively in the program was an 8-harness satin graphite fabric designated W-133 by Fiberite of 0.017-inch thickness and 24 x 23 warp/fill T300 (3K) yarn count. The graphite fabric was selected over unidirectional tape because (1) with the laboratory process used, it was easier to make fabric prepreg than to impregnate unidirectional tape, (2) a data base on polysulfone/graphite fabric and epoxy/graphite fabric exists to which data from this program could be compared, and (3) it is considerably easier to lay up the prepreg and maintain fiber alignment during laminate consolidation using fabric reinforcement.

#### 2.1.2 Polymer Characterization

The resin characterization procedures performed on PKXA .41 and Radel 5010 consisted of TGA, DSC, and IR. The TGA graphs (Fig. 2 and 3) indicate Radel 5010 to

|  |                    |      |                    |     |                      |             |
|--|--------------------|------|--------------------|-----|----------------------|-------------|
| SAMPLE:<br><br>PKXA .41<br><br>SIZE 10.8 mg. | X-AXIS             |      | Y-AXIS             |     | RUN NO. 2 DATE 19-78 |             |
|  | TEMP. SCALE 100 °C | inch | SCALE %            |     | OPERATOR D.L         |             |
|  | SHIFT 0            | inch | (SCALE SETTING X2) |     | HEATING RATE 5 °C    |             |
|  |                    |      | SUPPRESSION 0      | mg. | ATM. AIR             | .3 L/M min. |
|  |                    |      |                    |     | TIME CONSTANT 2      | sec.        |

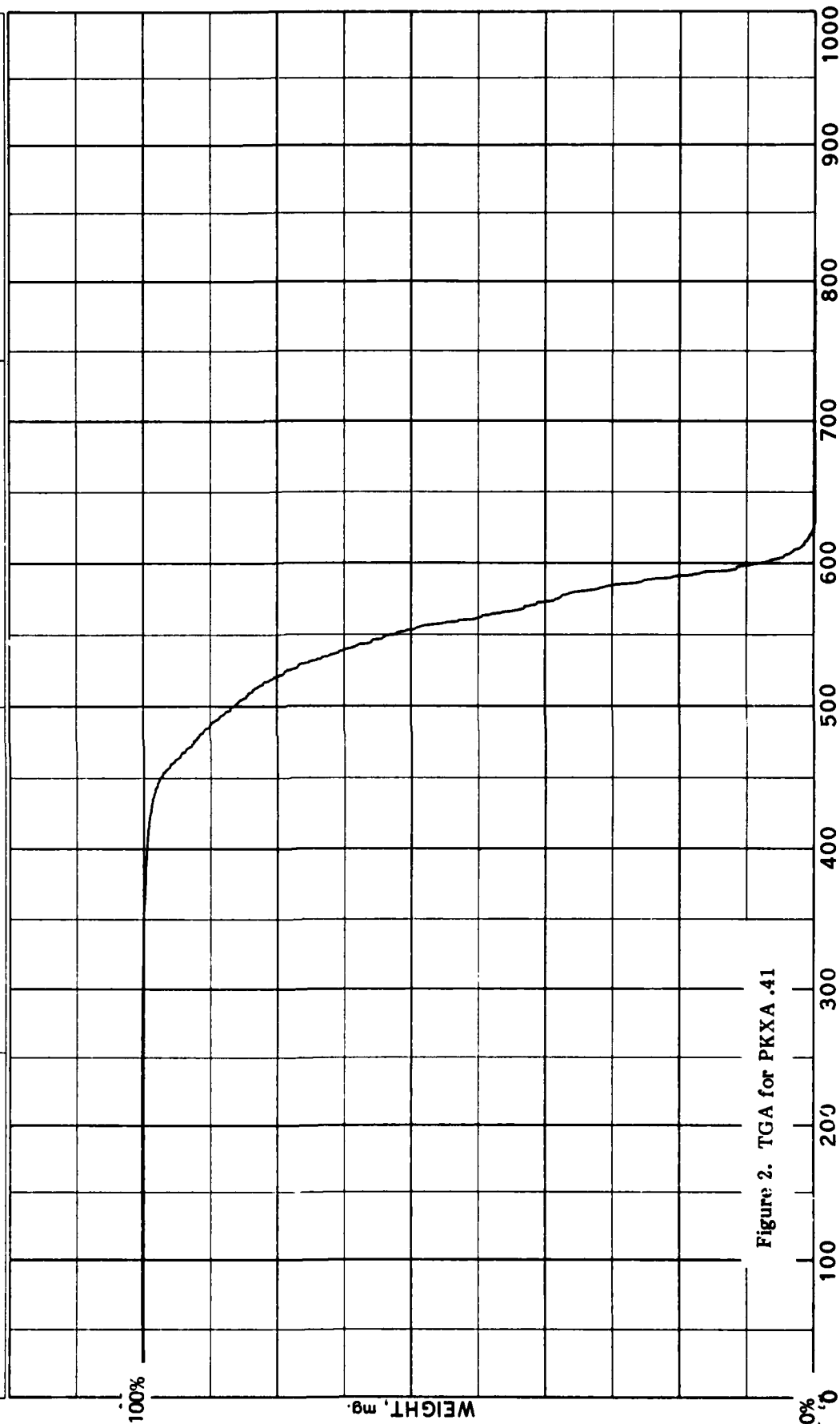


Figure 2. TGA for PKXA .41





# INSTRUMENTS

|  |                         |                     |             |                        |           |             |
|--|-------------------------|---------------------|-------------|------------------------|-----------|-------------|
| SAMPLE:<br><br>RADEL R 5010<br><br>SIZE 23.7 mg. | X-AXIS                  |                     | Y-AXIS      |                        | RUN NO. 1 | DATE 1-9-77 |
|  | TEMP. SCALE 100 °C/inch | SCALE %             | OPERATOR DL | HEATING RATE 5 °C/min. |           |             |
|  | SHIFT 0 inch            | (SCALE SETTING X 2) |             | ATM. AIR .3 L/M        |           |             |
|  |                         | SUPPRESSION 0 mg.   |             | TIME CONSTANT 2 sec.   |           |             |

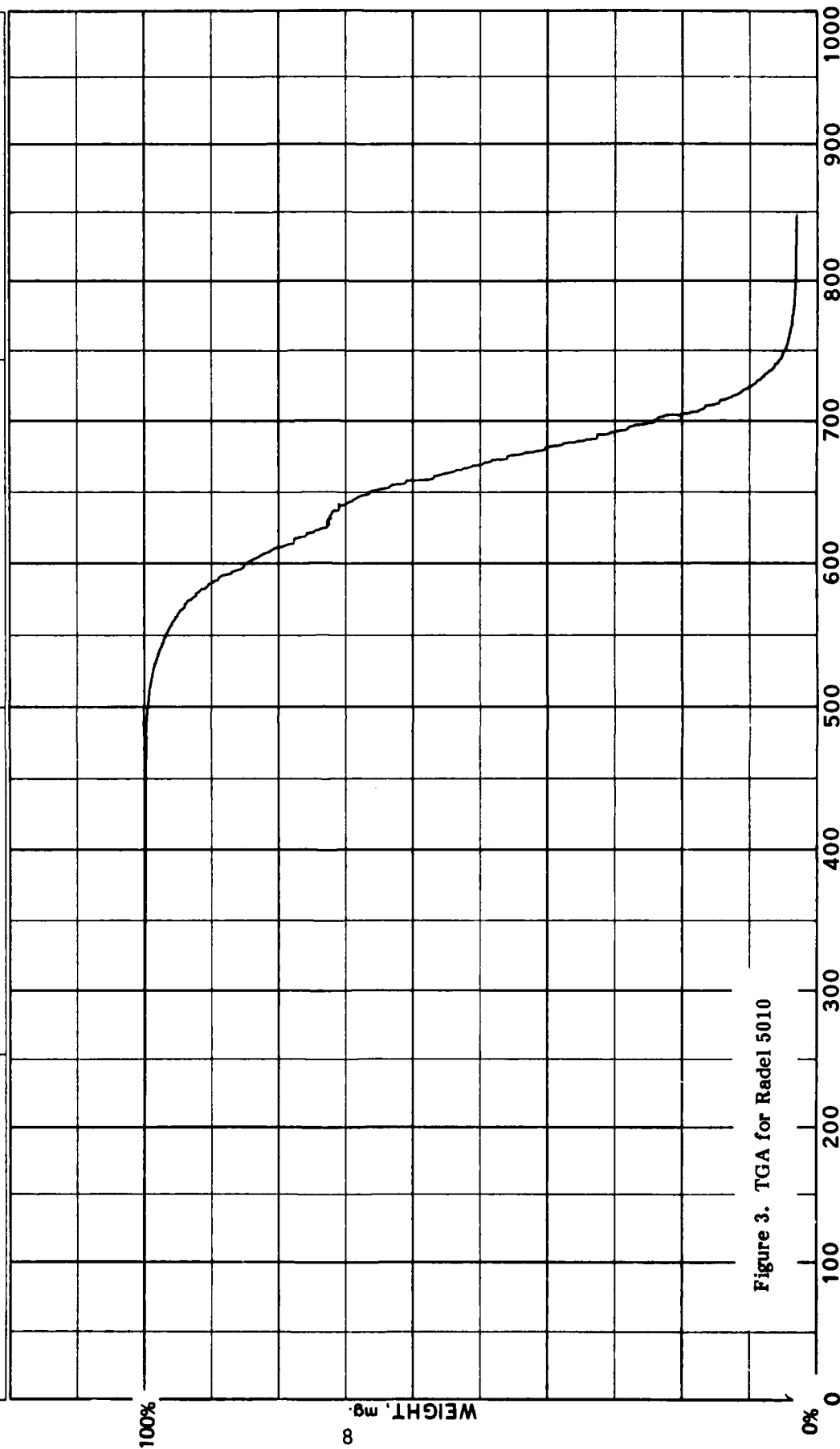


Figure 3. TGA for Radel 5010

T. °C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

be more thermally stable than PKXA .41 with initial weight loss and thermal decomposition temperatures occurring at 480 and 560°C, respectively, for Radel 5010, whereas they are 380 and 440°C for PKXA .41. In the DSC analysis (Fig. 4 and 5), softening begins at 180°C for PKXA .41 and at 220°C for Radel 5010. The exothermic response of PKXA .41 (Fig. 5) is attributed to polymer crosslinking, but no such response is seen for Radel 5010 (Fig. 4). The IR scans for PKXA .41 and Radel 5010 are presented in Figures 6 and 7, respectively.

### 2.1.3 Process Development

This portion of the program was composed of developing techniques for impregnating the graphite fabric with the thermoplastic resin and establishing optimum press molding cycles of the prepreg as determined by interlaminar shear and flexural properties of the consolidated laminates. All process development was conducted at Boeing using conventional equipment without modifications.

#### 2.1.3.1 Preimpregnation Process

After contacting several material suppliers, it became apparent that cost and schedule risks would be minimized by impregnating the graphite in-house at Boeing. This was accomplished using standard solvent impregnation techniques except for the graphite/CM-1 system. The CM-1 material was supplied in film form which was interplied between the graphite fabric and then press molded into laminates of the desired thickness.

The Radel 5010, 300P, and KM-1 resins were received in pellet form as shown in Figures 8, 9, and 10, respectively. The PKXA resins (Fig. 11) as received, were in the form of fluffy white flocs somewhat similar, physically, to Cab-O-Sil. The CM-1 was supplied as a transparent film that was interplied with graphite fabric as shown in Figure 12 prior to laminating. Film thickness of the CM-1 was 0.002 to 0.004 inch.

The processes for preparing prepreg with the Radel 5010, PKXA, 300P, and KM-1 were all similar. The graphite fabric/Radel 5010 prepregging process will be described in detail and differences between it and the processes used with the other resins will be identified. A piece of Fiberite W133 graphite fabric approximately 20 x 30 inches in size was weighed, placed on FEP film, and then attached to a piece of plywood with the FEP film located between the graphite fabric and the plywood. A hot, saturated solution of Radel 5010/dimethylformamide (DMF) was then swept into the fabric using

PART NO. 990069

RUN NO 1 DATE 1-8-78

OPERATOR D.L.

SAMPLE: PKXA .41

ATM. AIR

FLOW RATE

T-AXIS

SCALE: °C/in

PROG. RATE: °C/min 10

HEAT COOL ISO

SHIFT, in

TIME BASE, min/in

DTA-DSC

SCALE: °C/in

(mcal/sec)/in

WEIGHT, mg 7.80

REFERENCE GLASS BEADS

COVERED-VENTED

TGA

SCALE, mg/in

SUPPRESSION, mg

WEIGHT, mg

TIME CONST., sec

dY, (mg/min)/in 400

TMA

SCALE, mils/in

MODE

SAMPLE SIZE

LOAD, g

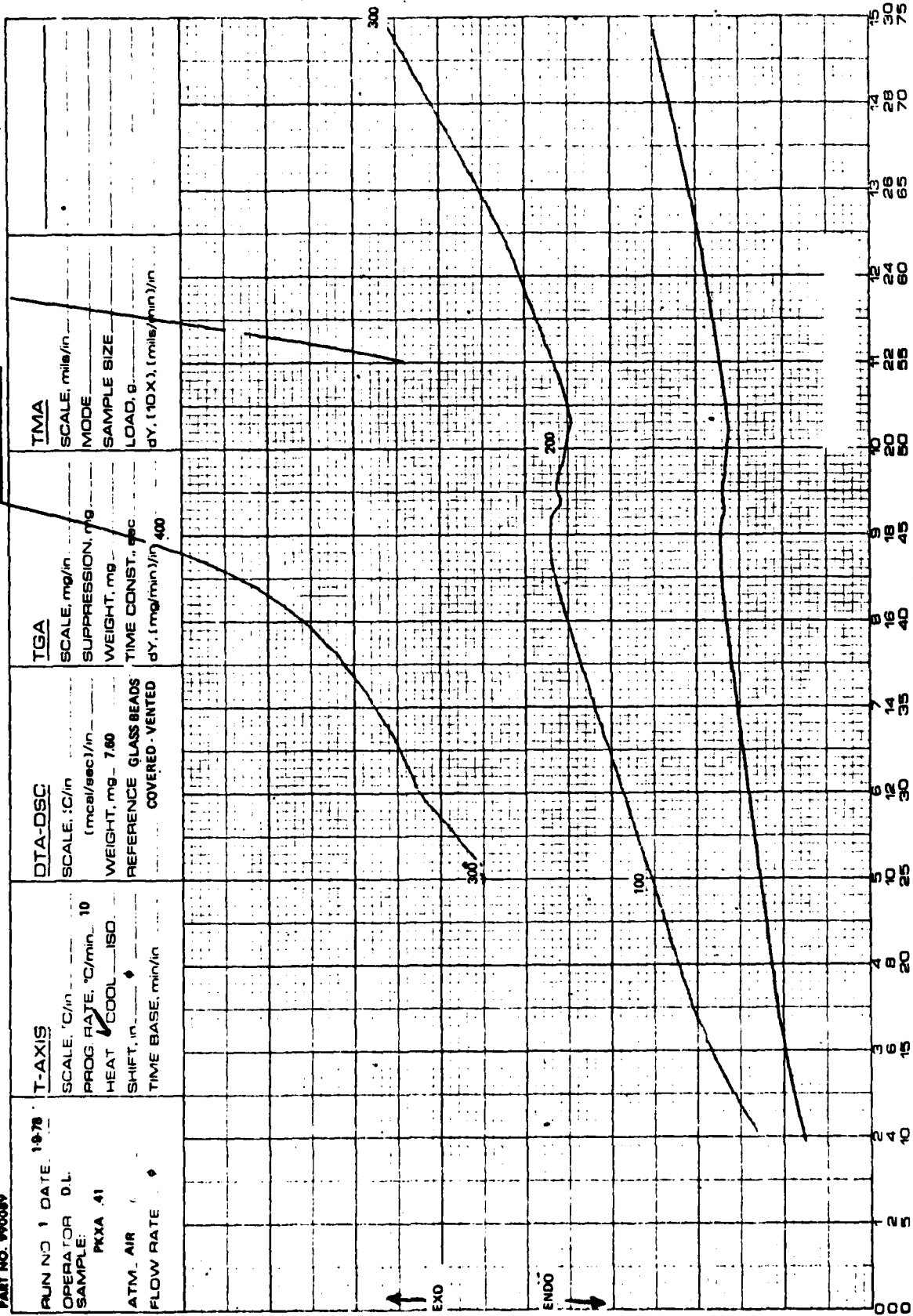
dY, (10X), (mils/min)/in

DUPONT Instruments

10

MEASURED VARIABLE

Figure 4. DSC for PKXA .41



PART NO. 990389

|  |  |  |  |  |  |   |  |  |  |
|--|--|--|--|--|--|---|--|--|--|
| <b>RUN NO. 1</b><br><b>DATE 10-78</b><br><b>OPERATOR D.L.</b><br><b>SAMPLE RADEL 5010</b><br><b>ATM. AIR</b><br><b>FLOW RATE 5</b><br><b>OPC</b> |  | <b>T-AXIS</b><br><b>SCALE: °C/in 20</b><br><b>PROG RATE: °C/min 10</b><br><b>HEAT COOL ISO</b><br><b>SHIFT. in 0</b><br><b>TIME BASE: min/in</b> |  | <b>DTA-DSC</b><br><b>SCALE: °C/in</b><br><b>(mcal/sec)/in</b><br><b>WEIGHT, mg 13.80</b><br><b>REFERENCE GLASS BEADS</b> |  | <b>TGA</b><br><b>SCALE: mg/in</b><br><b>SUPPRESSION, mg</b><br><b>WEIGHT, mg</b><br><b>TIME CONST., sec</b><br><b>dY, (mg/min)/in</b> |  | <b>TMA</b><br><b>SCALE: mils/in</b><br><b>MODE</b><br><b>SAMPLE SIZE</b><br><b>LOAD, g</b><br><b>dY, (10 X), (mils/min)/in</b> |  |
|--|--|--|--|--|--|---|--|--|--|

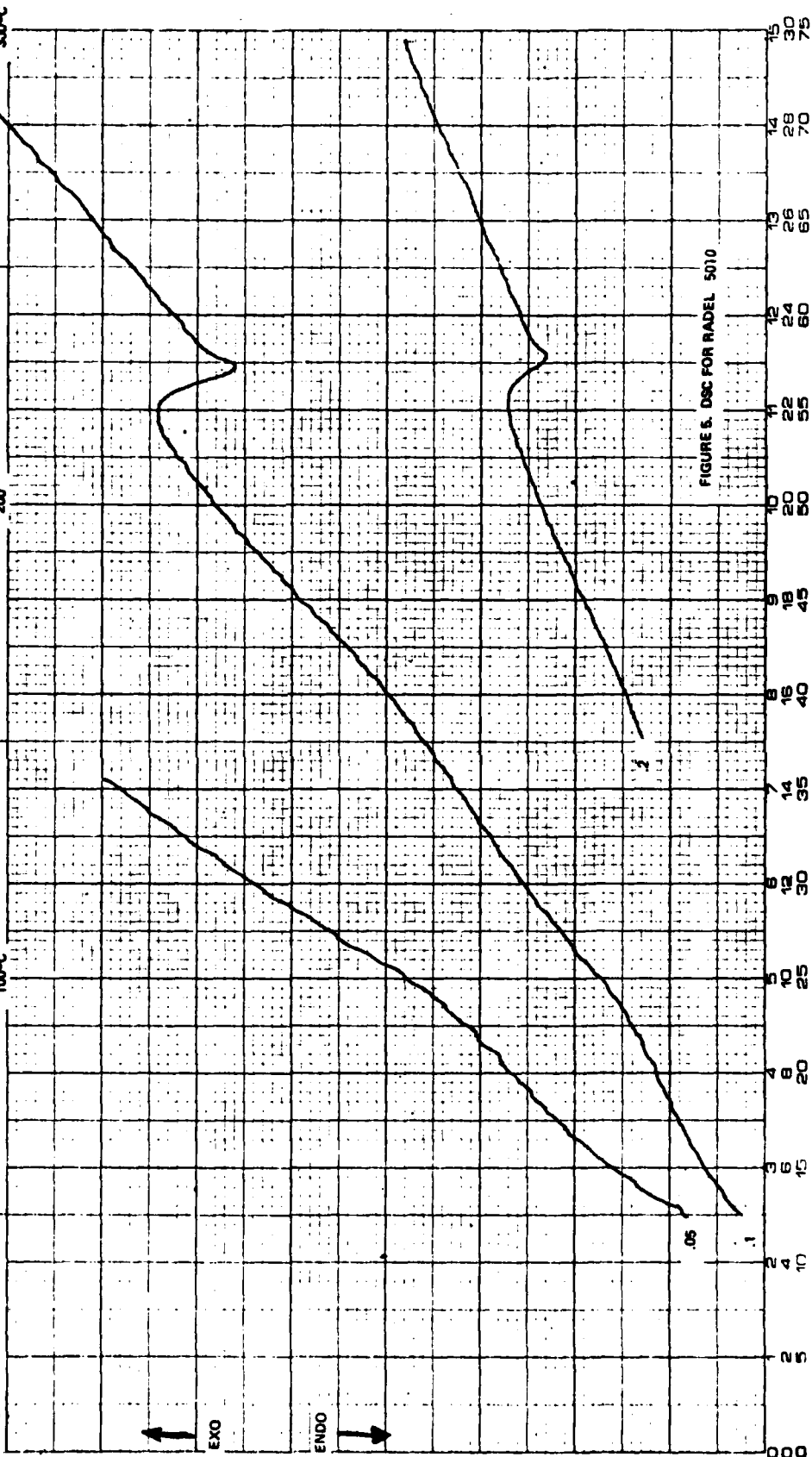


Figure 5. DSC for RADEL 5010

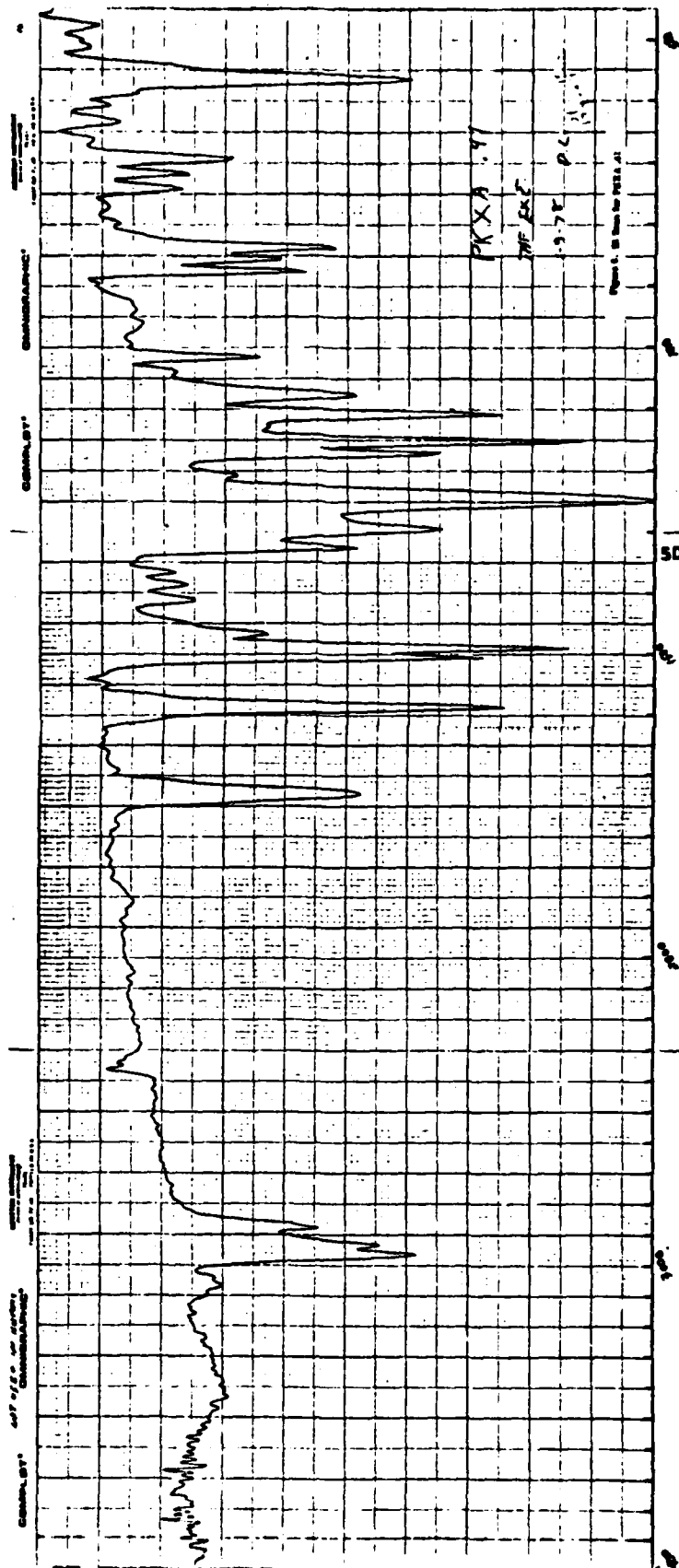


Figure 6. IR Scan for PKXA .41

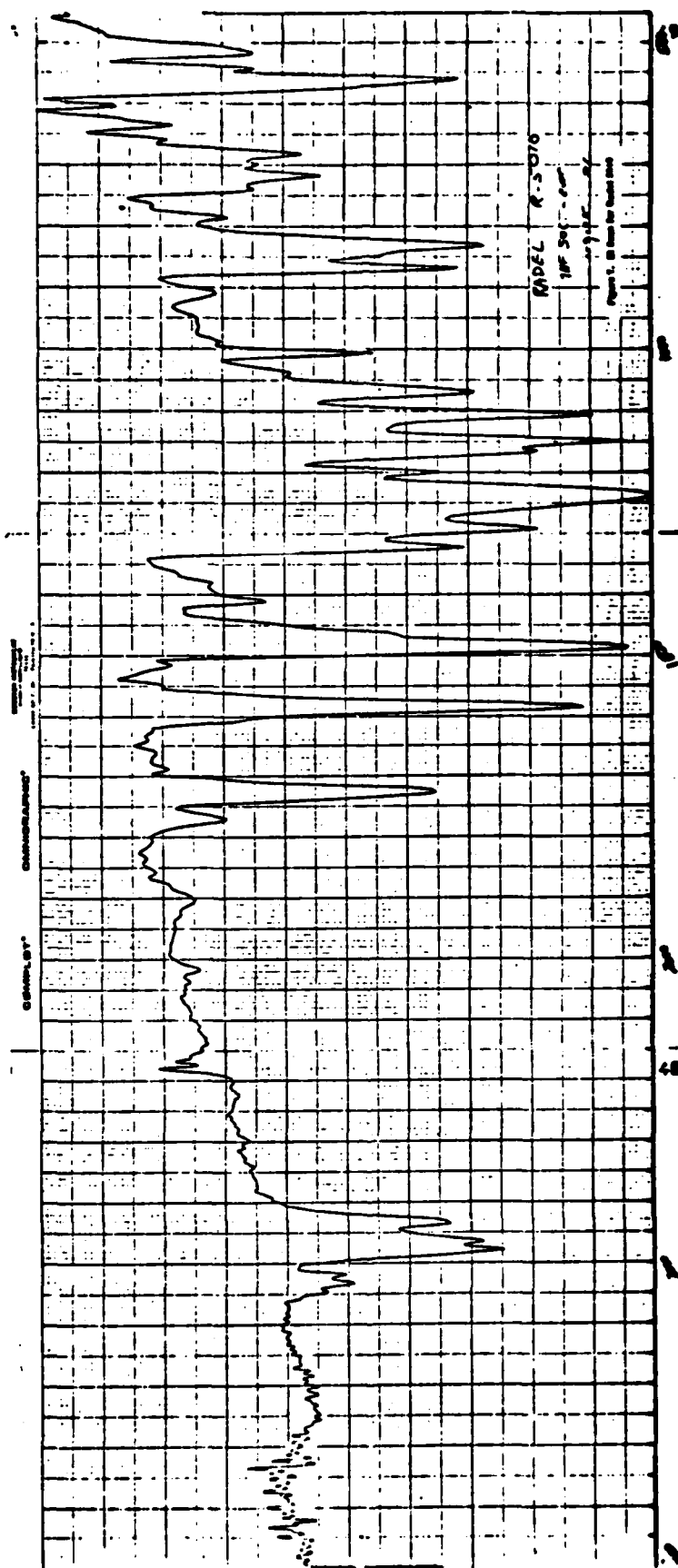


Figure 7. IR Scan for Radel 5010

**RADEL 5010**



RADEL 5010 RESIN  
FIGURE 8



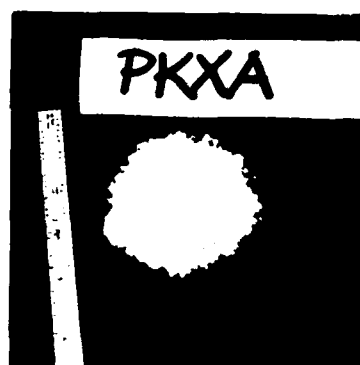
**300P**

300 P RESIN  
FIGURE 9

**KM-1**



KM-1 RESIN  
FIGURE 10



PXKA RESIN  
FIGURE 11

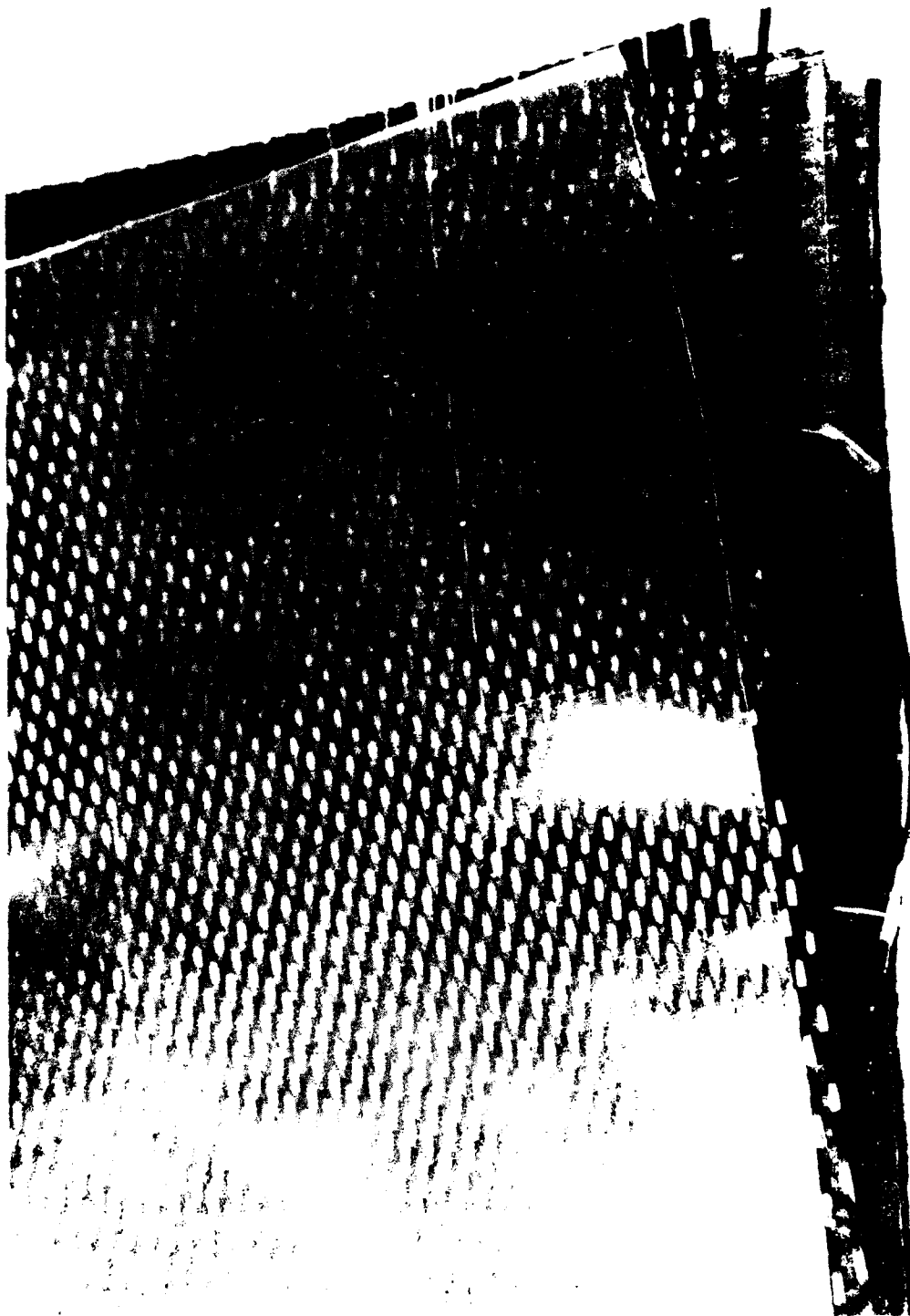


Figure 12: CM-1 INTERPLIED WITH GRAPHITE FABRIC



a Teflon sweep as shown in Figure 13. This operation was accomplished in a vented hood. The Radel 5010 coated fabric was dried using a quartz lamp for 1 to 2 hours and then was turned over and the other side coated in a similar manner. This procedure was repeated until both sides of the fabric had been coated three or four times. The prepreg was weighed and the resin/residual solvent content calculated. If the resin/residual solvent content was less than 35%, additional coats were applied. The prepreg was then dried in an air-circulating oven at 300°F for 2 hours, cooled, weighed, and the final resin content calculated. A piece of prepreg prepared in this manner is shown in Figure 14, which also shows the stiff, boardy nature of thermoplastic matrix prepreps.

A similar procedure was used to prepare the PKXA, KM-1, and 300P prepreps with changes incorporated to accommodate the particular characteristics of each system. Particulars are given in Table I.

#### 2.1.3.2 Molding Cycle Development

During this part of the program, the laminating parameters of time, temperature, and pressure for each system were established. While these parameters did turn out to be within the capabilities of many autoclaves, it is appropriate to mention that, unlike other composite materials, thermoplastic matrix composite laminating parameters are not restricted by autoclave limitations. The reason for this is that the low-cost fabrication potential of thermoplastic composites is best achieved using in-hot, out-hot molding cycles not possible with autoclaves.

The molding (consolidating) of prepreg into laminates was accomplished in a Pasadena Hydraulic Press of 800°F upper temperature capability. Prior to selecting a molding cycle, the melt behavior and observed viscosity changes of each resin with increasing temperature were examined using a Fischer-Johns melting point apparatus. By this technique, the molding temperature to be used on the first attempt at molding laminates with each system was established.

Selection of the other primary laminating parameter, pressure, was based upon previous experience (ref. 1-5) and the physical characteristics of each resin. Laminating pressures used ranged from 200 to 400 psi. This range is adequate for compacting the prepreg without damaging the reinforcement or causing excessive resin flow.



Figure 13: PREPREG PREPARATION

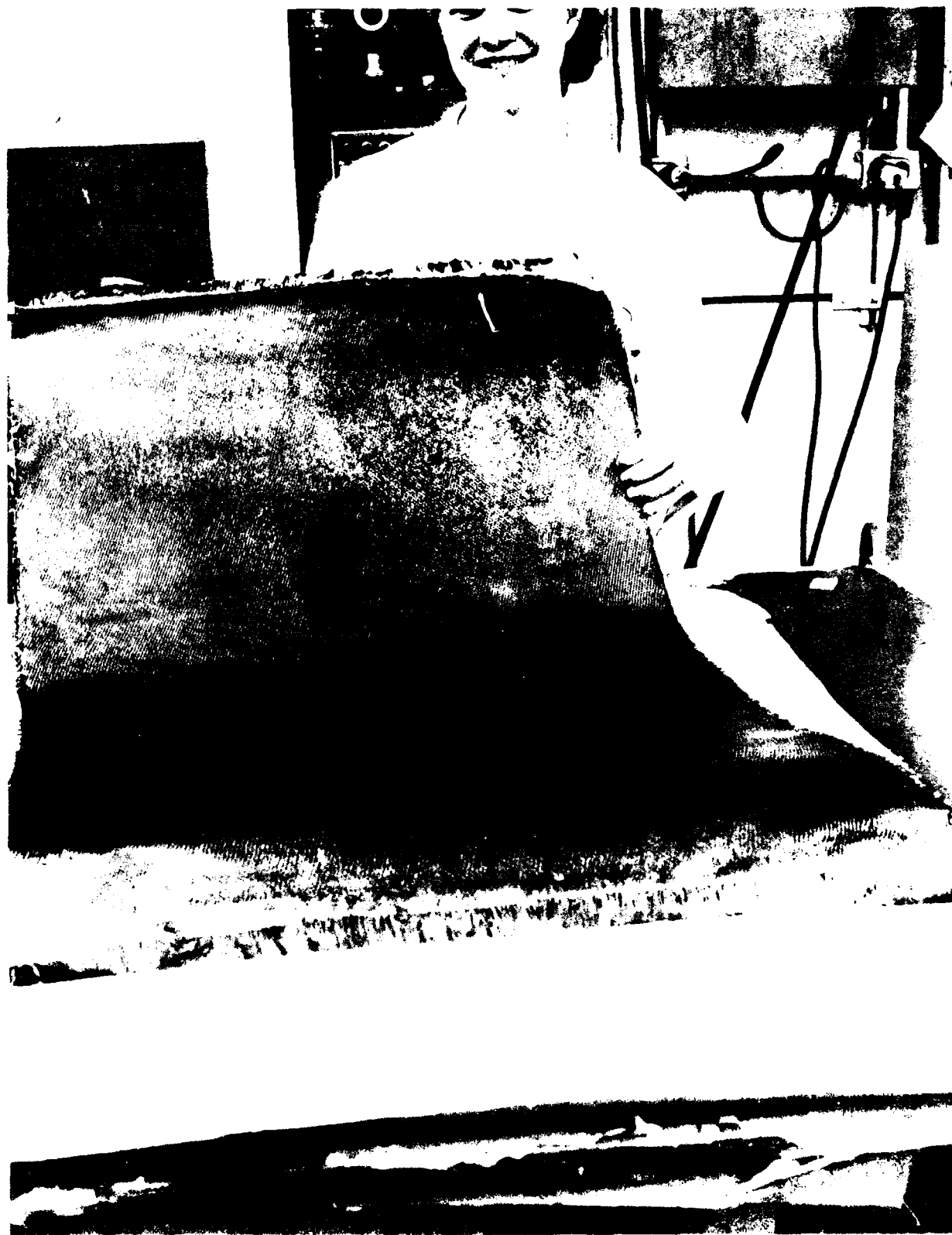


Figure 14: RADEL 5010 PREPREG

TABLE I—PREPREGGING PARAMETERS

| Resin                        | Impregnation Method   | Drying Cycle  |
|------------------------------|---|---|
| PKXA .41<br>and<br>PKXA .517 | Solvent impregnation<br>from methylene<br>chloride            | The prepregged sheets were air dried at RT for a minimum of 2 hours and then force-air dried in an oven at 250°F for 2 hours. The oven temperature was raised from RT to 250°F very slowly to prevent the polymer from blistering or bubbling on the outer surface of the fabric. The drying temperature was limited to 250°F to prevent excess cross-linking of the polymer prior to the molding cycle.        |
| 300P                         | Solvent impregnation<br>from hot dimethyl-<br>formamide (DMF) | The 300P prepreg sheets were initially dried in the hood with quartz heat lamps used for the impregnation process. After the final coat of resin was applied to the prepreg, the solvent was removed from the prepreg with the quartz lamps and then hung in an oven to complete the drying cycle. The temperature of the oven was raised very slowly to 350°F to prevent blistering and bubbling of the resin. |
| KM-1                         | Solvent impregnation<br>from hot dimethyl-<br>formamide (DMF) | See cycle for 300P above.   |
| CM-1                         | Hot melt from<br>thin film                                    | The CM-1 film did not require a drying cycle for solvent removal. The material was weighed and interplied between the graphite fabric plies (Fig. 12), vacuum bagged, and placed into the press. The press temperature was raised from RT to 620°F and held at temperature for 45 minutes without pressure to impregnate the fibers prior to starting the molding cycle.  |

The prepreg layup and bagging operations prior to press cure will now be described. Since the quality of the laminate would be determined by short beam shear and flexure testing, seven plies of prepreg were used to obtain the proper laminate thickness. The prepreg plies were cut to size and laid up as shown in Figure 15. Several spot welds made with a soldering iron were usually used to keep the plies aligned. The prepreg was then envelope-bagged as shown schematically in Figure 16. In Figure 17, the layup has been positioned in the vacuum bag and Figure 18 shows the bagged assembly ready for insertion into the press (Fig. 19). A cured 300P laminate and portions of prepreg from which it was made are shown in Figure 20.

While high-rate production processes do not require the part to be vacuum bagged, this bagging procedure was used during this process development study to reduce the number of variables that had to be evaluated.

The molding cycle particulars for each system follow:

#### Radel 5010

The Radel 5010 materials were bagged as shown in Figure 16, then placed in a press at room temperature. The temperature was raised from room temperature to 745°F and held at 745°F for 1/2 hour to allow the resin to completely wet out the graphite fibers. Following the 1/2-hour soak, 200 psi pressure was applied to the part and the part was allowed to reach equilibrium, held for an additional 1/2 hour, and cooled under pressure.

#### CM-1

The CM-1 molding cycle was a continuation of the prepreg impregnation cycle that was previously described in Table I. Following the 45-minute impregnation at 620°F in the press, 200 psi pressure was applied to the bagged parts and then the part was held at temperature and pressure for an additional 45 minutes and cooled. Note: the molding temperature must be 625°F or below to prevent decomposition of the polymer being processed. When CM-1 resins are heated to processing temperatures, gaseous decomposition products are released. To prevent their inhalation, ovens and processing equipment must be vented and adequate ventilation provided in the working area. Waste should be buried, not burned, since decomposition products resulting from burning CM-1 resins are harmful when inhaled.



Figure 15: PREPREG PLIES PRIOR TO CONSOLIDATION

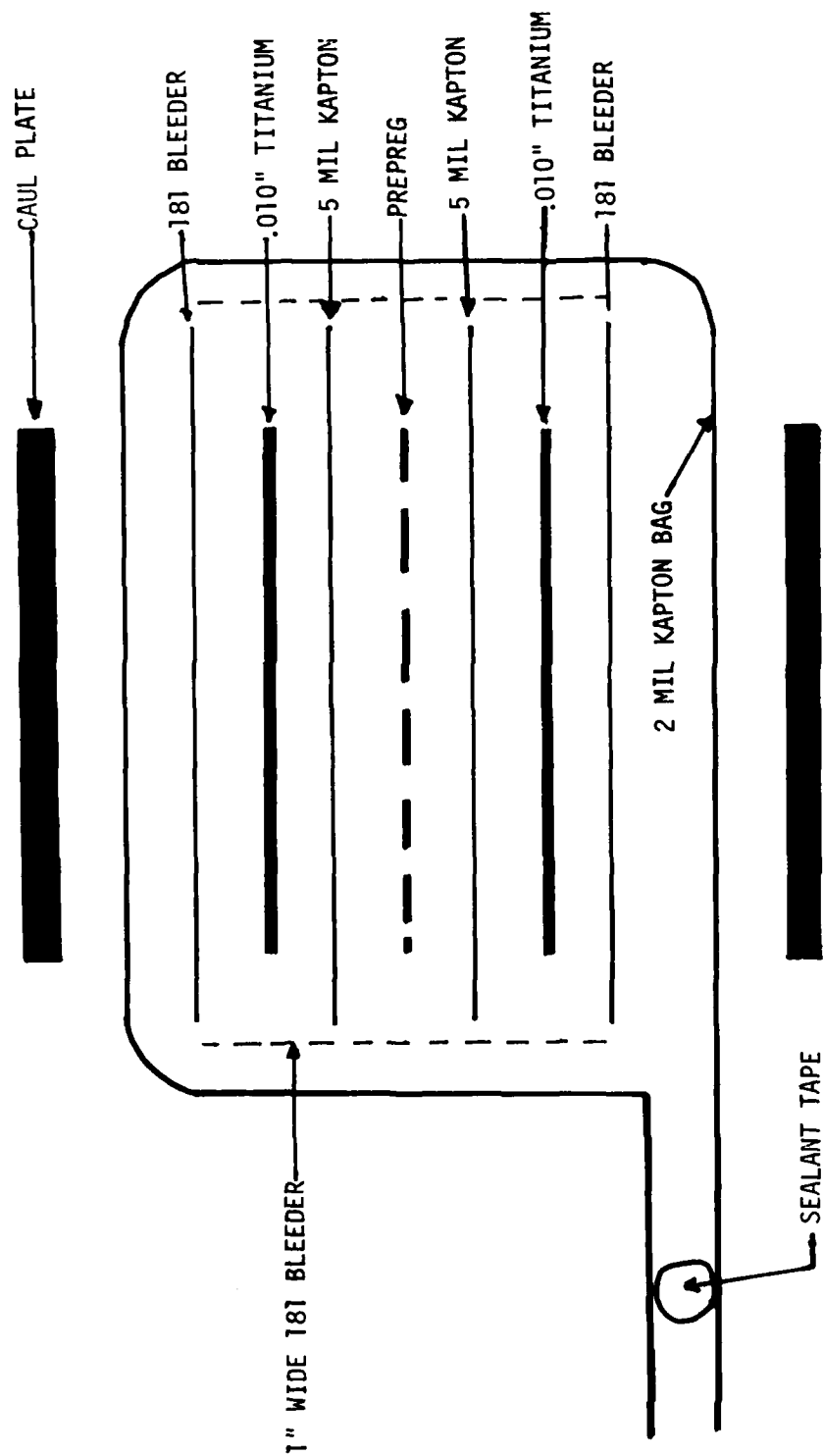


FIGURE 16. BAGGING SCHEMATIC

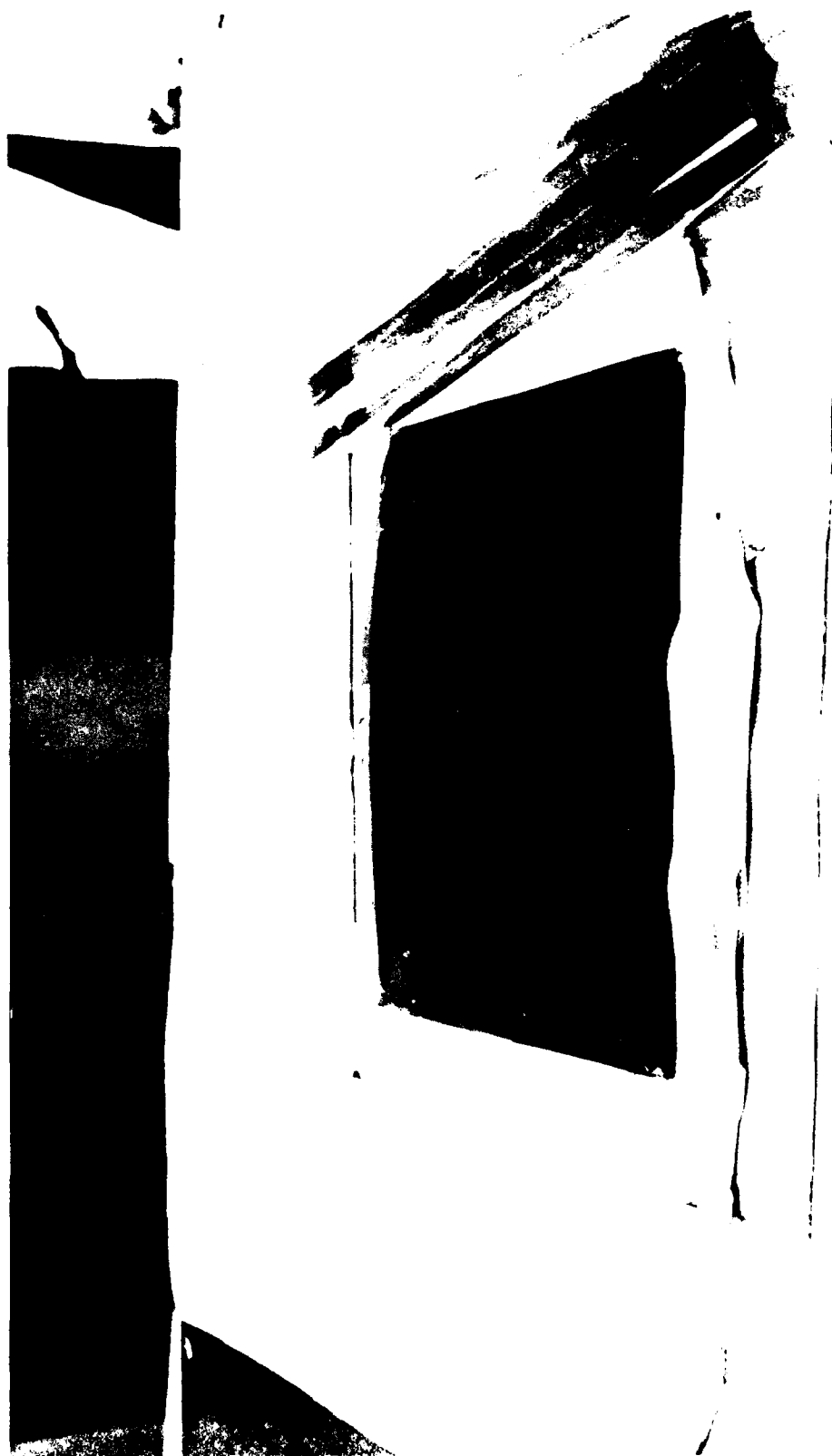


Figure 17: APPLYING THE VACUUM BAG





Figure 18: BAGGED ASSEMBLY READY FOR PRESS MOLDING

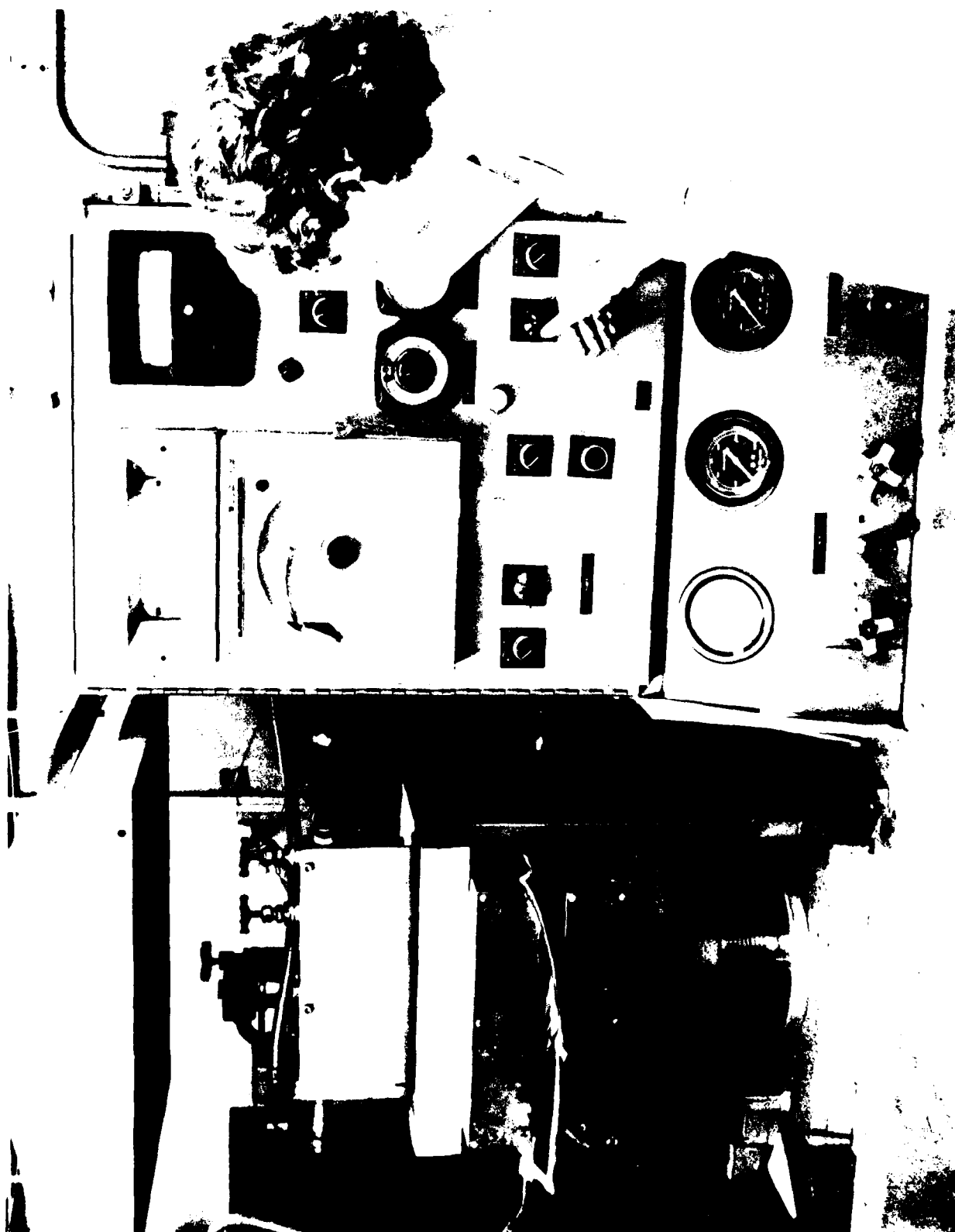


Figure 19: PRESS MOLDING THE LAMINATE

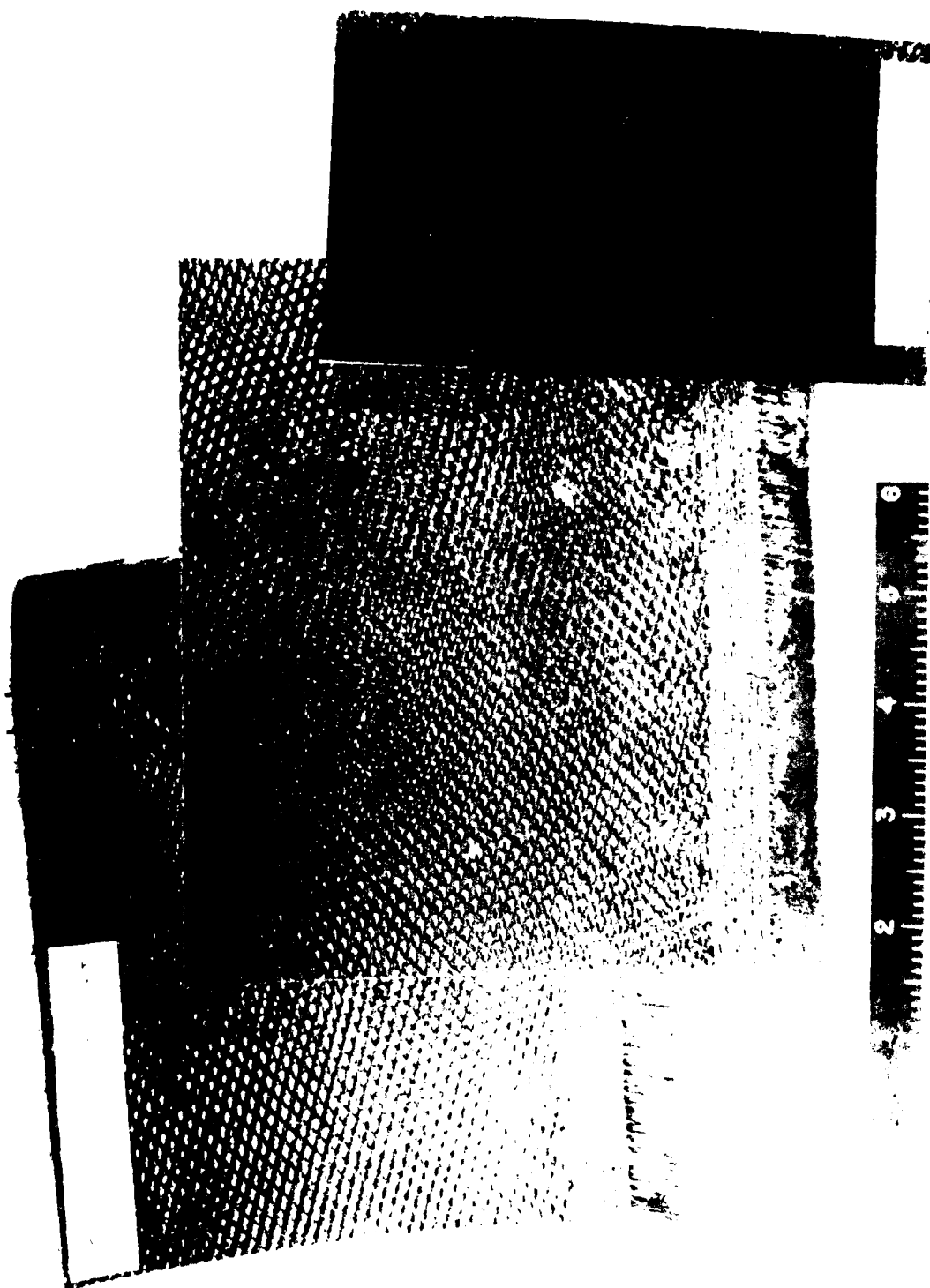


Figure 1: 40 PLY EPOXY AN LAMINATE

### 300P

Two molding cycles for 300P resin were used in fabricating laminates. The first molding cycle consisted of placing the prepreg in a vacuum bag under full vacuum in a 600°F preheated press, applying 200 psi pressure, and increasing the temperature to 745°F and holding for 45 minutes prior to cooling. This cycle was not acceptable because the high temperature seemed to start breaking down the polymer (detected by foul odor) and the Kapton film failed to release from the cured laminate.

The second molding cycle consisted of vacuum bagging and heating the prepreg in a press from room temperature to 350°F, holding the part at 350°F for 45 minutes to remove the last traces of solvent, and then increasing the heat to 640°F for 2 hours, applying 200 psi pressure, holding for 45 minutes, and cooling under pressure.

### KM-1

The first molding cycle consisted of vacuum bagging and heating in a press from room temperature to 450°F with a 30-minute hold at 450°F, applying 200 psi pressure, and increasing the temperature to 650°F for 30 minutes before cooling under pressure. This cycle allowed too much washout of resin from the laminate and complete delamination of the panel occurred during cutting.

In the second molding cycle, the prepreg was vacuum bagged and heated in a press from room temperature to 450°F, held for 1/2 hour, and then heated to 600°F for 30 minutes. Pressure of 200 psi was applied and the part was held at temperature and pressure for 15 minutes prior to cooling under pressure.

### PKXA

The layup was bagged and placed into a cold press. The temperature was increased to 225°F, held for 45 minutes (to drive off any remaining solvents), and then 200 psi pressure was applied to the part. The part temperature was then increased to 650°F, held for 30 minutes, and the part cooled under pressure.

The second molding cycle was essentially the same, except that 400 psi pressure was applied to the part.

#### 2.1.4 Mechanical Properties

Flexural, interlaminar shear (short beam method), tension, and compression properties were determined on graphite fabric reinforced laminates processed as described in Section 2.1.3. All specimens were machined from laminates of seven-ply thickness except that the tension specimens were taken from five-ply laminates. Specimen configuration is shown in Figures 21 through 25.

Tension, interlaminar shear, flexure, and compression specimens were tested per ASTM standards D638, D2344, D790, and D695, respectively. A 2-inch span was used in testing the flexure specimens and a 4-to-1 span-to-depth ratio was used on the interlaminar shear specimens. Three-point loading was used for testing both the flexure and interlaminar shear specimens.

Test temperatures of 75, 250, 350, and 400°F were used.

The test results (Table II) obtained on Radel 5010 composite specimens are comparable to P1700 polysulfone properties. Of particular interest is the good retention of Radel 5010 properties at 250 and 350°F.

Two PKXA polymers were evaluated during the process development studies of Task I. These polymers were PKXA .41 and PKXA .517. The mechanical test results were lower than obtained previously (ref. 3). It was discovered that PKXA materials had large quantities of jelled material in the solutions of polymer and methylene chloride. The presence of this jelled polymer was absent from the PKXA .41 material initially; however, some jelled material was present in the initial solution of PKXA .517. Prior to processing, the jelled material was strained from the impregnating solution and discarded. It is believed that the polymer was crosslinking upon standing in solution prior to solvent impregnation of the graphite fabric. The test results from the PKXA systems are presented in Table II.

Graphite composites fabricated with 300P polyethersulfone also exhibited good laminate properties at 75, 250, and 350°F. The 400°F tests of the 300P composites showed good tensile properties, but the compression, flexure, and shear strengths were reduced 50% from room-temperature results. These data are also presented in Table II.

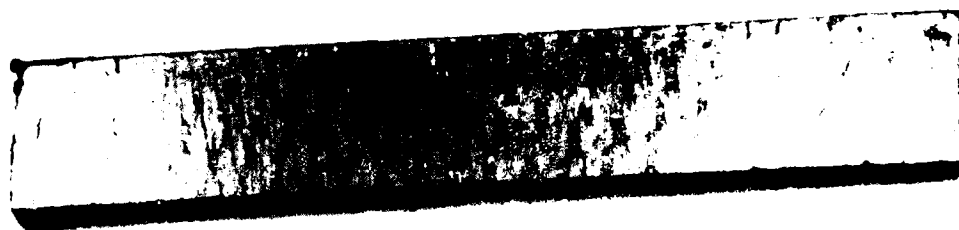
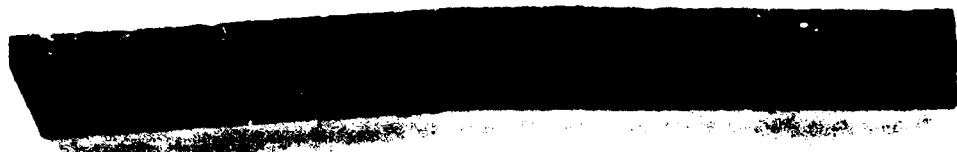


Figure 21: FEDERAL DEPT. OF JUSTICE

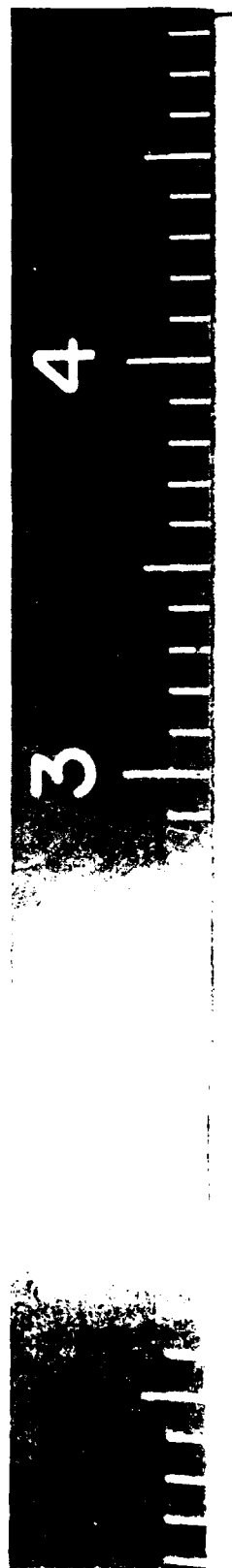


Figure 22: SHORT BEAM SHEAR SPECIMENS

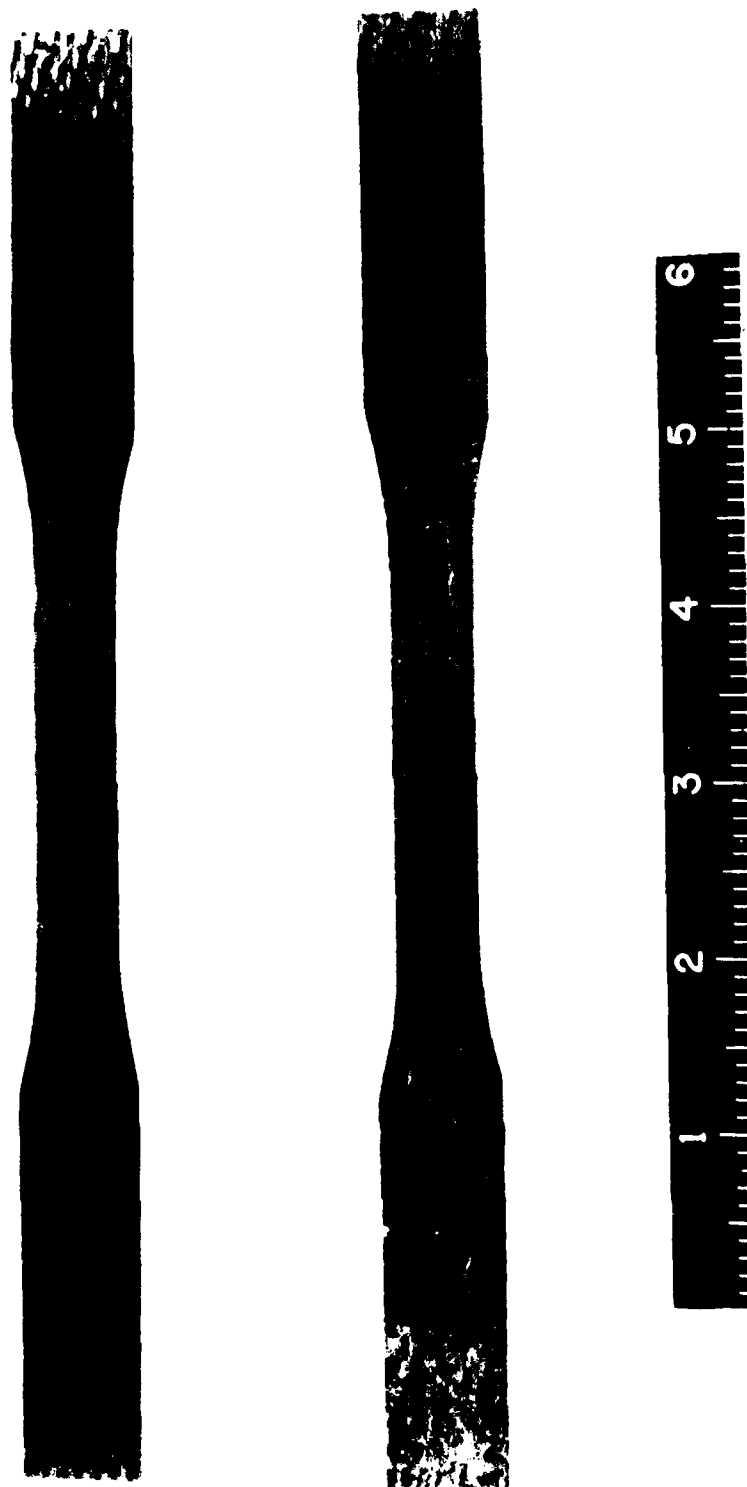


Figure 23: TENSION SPECIMENS BEFORE TEST





Figure 24: TENSION SPECIMENS AFTER TEST

TABLE II--BASELINE MECHANICAL PROPERTIES--TASK I

| Laminate   | Temperature<br>of | Tension         |                |                 | Compression    |                 |                | Flexural        |                |                 | Shear<br>Strength<br>ksi |
|------------|-------------------|-----------------|----------------|-----------------|----------------|-----------------|----------------|-----------------|----------------|-----------------|--------------------------|
|            |                   | Strength<br>ksi | Modulus<br>msi | Strength<br>ksi | Modulus<br>msi | Strength<br>ksi | Modulus<br>msi | Strength<br>ksi | Modulus<br>msi | Strength<br>ksi |                          |
| Radel 5010 | 75                | 63.6            | 8.3            | 60.5            | 8.1            | 102.3           | 8.1            | 7.7             |                |                 | 7.7                      |
|            | 250               | 59.3            | 7.6            | 53.9            | 7.3            | 84.9            | 7.7            | 5.4             |                |                 | 5.4                      |
|            | 350               | 51.4            | 6.3            | 47.5            | 5.9            | 66.7            | 5.1            | ---             |                |                 | ---                      |
|            | 400               | 35.2            | 4.9            | 34.8            | 4.1            | 39.9            | 4.1            | 2.4             |                |                 | 2.4                      |
| PKXA .41   | 75                | 42.8            | 8.2            | 39.8            | 8.1            | 61.9            | 7.0            | 4.3             |                |                 | 4.3                      |
|            | 250               | 41.2            | 10.2           | 34.1            | 7.5            | 49.1            | 6.9            | 3.2             |                |                 | 3.2                      |
|            | 350               | ---             | ---            | ---             | ---            | 11.5            | ---            | ---             |                |                 | ---                      |
|            | 400               | 28.3            | 5.8            | 23.7            | 4.9            | 6.2             | 4.5            | 1.0             |                |                 | 1.0                      |
| PKXA .517  | 75                | 47.2            | 7.3            | 43.5            | 7.9            | 62.0            | 6.7            | 4.9             |                |                 | 4.9                      |
|            | 250               | 42.6            | 6.9            | 38.4            | 7.2            | 43.5            | 6.4            | 3.6             |                |                 | 3.6                      |
|            | 350               | 39.2            | 6.2            | 34.0            | 6.9            | 10.1            | 5.7            | 1.6             |                |                 | 1.6                      |
|            | 400               | 31.2            | 6.1            | 29.4            | 5.1            | 4.0             | 4.2            | ---             |                |                 | ---                      |
| 300P       | 75                | 70.7            | 8.2            | 70.8            | 9.3            | 89.0            | 8.6            | 6.8             |                |                 | 6.8                      |
|            | 250               | 57.1            | 7.1            | 53.7            | 8.7            | 56.3            | 5.9            | 4.4             |                |                 | 4.4                      |
|            | 350               | 49.8            | 7.1            | 47.5            | 8.7            | 53.9            | 5.4            | ---             |                |                 | ---                      |
|            | 400               | 47.5            | 5.7            | 28.2            | 8.8            | 34.9            | 4.7            | 2.5             |                |                 | 2.5                      |
| KM-1       | 75                | ---             | ---            | ---             | ---            | 60.0            | 8.6            | 3.8             |                |                 | 3.8                      |
|            | 75                | ---             | ---            | ---             | ---            | 67.1            | 9.5            | 4.0             |                |                 | 4.0                      |
|            | 75                | ---             | ---            | ---             | ---            | 121.7           | 11.1           | ---             |                |                 | ---                      |
| CM-1       | 75                | ---             | ---            | ---             | ---            | 54.0            | 5.6            | 4.9             |                |                 | 4.9                      |
|            | 75                | ---             | ---            | ---             | ---            | 64.9            | 6.8            | 7.0             |                |                 | 7.0                      |
|            | 75                | ---             | ---            | ---             | ---            | 85.3            | 8.54           | 6.5             |                |                 | 6.5                      |

Preliminary test data were obtained from the evaluation of a new polyethersulfone. This material, designated KM-1, was manufactured by ICI Americas, Inc. The graphite/ KM-1 laminates were evaluated for flexural strength, interlaminar shear strength, and solvent resistance to common laboratory solvents that affect other thermoplastic materials. The test data obtained from this evaluation of KM-1 materials are presented in Table II. Test data show that KM-1 has potential of properties equivalent to P1700 polysulfone, 300P polyethersulfone, and Radel 5010 polyphenylsulfone materials, but additional process development is needed.

A new high-performance fluoropolymer (CM-1) from Allied Chemical Corporation was evaluated as a matrix material for advanced thermoplastic composites. The material was evaluated for flexural strength, interlaminar shear strength, and solvent resistance. A summary of the mechanical test data is presented in Table II. The CM-1 resin shows promise of being a good matrix material and further process optimization studies appear warranted.

#### 2.1.5 Environmental Resistance

To determine the fluid resistance of the graphite/thermoplastic composites, unstressed and stressed (Fig. 26) flexure specimens were immersed in fluids common to aircraft operations. The fluids were JP-4 fuel, MIL-H-5606 hydraulic fluid, MIL-L-7808 synthetic lubricant, MIL-H-83306 hydraulic fluid, and salt water. Duration of fluid exposure was 28 days. The two systems evaluated were the graphite fabric reinforced Radel 5010 and 300P. Laminates prepared using the KM-1 and CM-1 resins, which were received too late in the program for complete evaluation, were tested for fluid resistance in the unstressed mode only.

As shown in Table III, the Radel 5010 composite specimens had excellent resistance to environmental aging solutions, with the exception of MIL-H-83306 hydraulic fluid. The Radel 5010 stressed specimens completely delaminated in the MIL-H-83306 hydraulic fluid and unstressed specimens were degraded by 29% of the initial control properties. The MIL-H-83306 hydraulic fluid (Skydrol) is not normally used in naval aircraft, but was included in this study because of its known aggressive attack on organic polymers. A 16% decrease in strength was noted for specimens that were immersed in MIL-L-7808 under stress, while a 12.2% decrease in strength was noted for the unstressed specimens.



Figure 25: COMPRESSION SPECIMENS

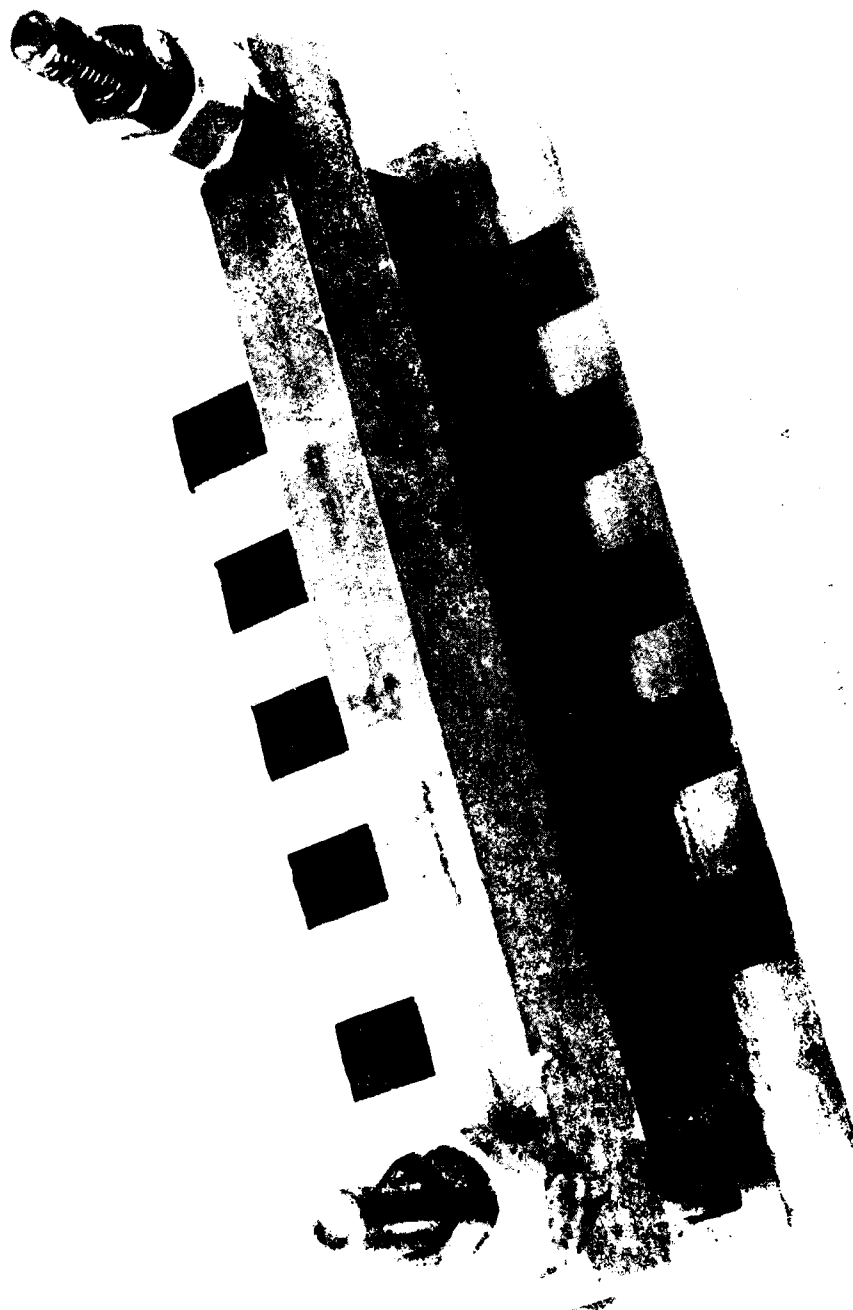


Figure 26: STRESSED FLEXURE SPECIMEN

TABLE III—ENVIRONMENTAL EXPOSURE—TASK I

| Exposure                       | Stress Level<br>% of Ultimate | Flexural                   |                            |                            |                            |
|--------------------------------|-------------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
|                                |                               | Str. x 10 <sup>3</sup> psi | Mod. x 10 <sup>6</sup> psi | Str. x 10 <sup>3</sup> psi | Mod. x 10 <sup>6</sup> psi |
| Radel 5010                     |                               |                            |                            |                            |                            |
| 300P                           |                               |                            |                            |                            |                            |
| Control                        | 0                             | 102.0                      | 9.2                        | 100                        | 12.1                       |
| JP-4 Fuel                      | 60                            | 94.2                       | 8.6                        | 1/                         | 1/                         |
| 28 days                        | 0                             | --                         | ---                        | 94.8                       | 8.9                        |
| MIL-H-5606 Hydraulic Fluid     | 60                            | 94.0                       | 8.8                        | 1/                         | 1/                         |
| 28 days                        | 0                             | 114.9                      | 9.2                        | 107.7                      | 9.1                        |
| MIL-L-7808 Synthetic Lubricant | 60                            | 85.8                       | 9.6                        | 1/                         | 1/                         |
| 28 days                        | 0                             | 89.6                       | 9.0                        | 76.3                       | 6.0                        |
| MIL-H-83306 Hydraulic Fluid    | 60                            | 1/                         | 1/                         | 1/                         | 1/                         |
| 28 days                        | 0                             | 71.4                       | 8.8                        | 85.9                       | 3.2                        |
| Salt Water Environment         | 60                            | 103.3                      | 9.4                        | 1/                         | 1/                         |
| 28 days                        | 0                             | 95.3                       | 9.2                        | 91.3                       | 7.0                        |
| 1/ Delaminated                 |                               |                            |                            |                            |                            |

1/ Delaminated

The 300P composite specimens also were immersed in fluid environments in both the stressed and unstressed conditions. The stressed specimens failed in all environments under 60% load (Table III). The stressed specimens that were immersed in salt water, JP-4, MIL-L-7808, and MIL-H-5606 delaminated between plies under the load points. Specimens that were immersed in MIL-H-83306 delaminated completely into a number of separate pieces of graphite fabric. These results were not anticipated, particularly since the unstressed specimens were not severely degraded by the same fluids. This apparent anomaly needs further study and verification.

To determine the resistance of KM-1 and CM-1 to solvent exposure, small (1/4 x 1/4 x 0.090-inch) pieces cut from tested flexure specimens were immersed in the same solvents as used in Table III plus one additional solvent, methylene chloride. These samples were visually examined periodically, with no degradation apparent after 30 days except for the KM-1 specimen immersed in methylene chloride which showed signs that the KM-1 resin was being degraded after 2 to 4 days exposure. It is appropriate to note that methylene chloride also degrades epoxy matrix laminates. These preliminary findings indicate that the KM-1 and CM-1 resins are two of the most solvent-resistant resins evaluated and further fluid resistance studies under stressed and unstressed conditions should be performed.

## 2.2 TASK II—METAL CLAD COMPOSITES

The application of a thin metal cladding to exterior composite surfaces offers improved scuff resistance, provides lightning-strike protection, and also provides an impervious barrier to fluid. The thermoplastic resins evaluated in this program are more resistant to fluids than polysulfone and it was felt that metal cladding would improve their fluid resistance even more.

In Task II, two of the composite systems evaluated in Task I were clad with 0.010-inch-thick titanium and tested for mechanical properties and fluid resistance. Postforming studies were performed and the effect of thermal cycling also was determined on the selected systems.

### 2.2.1 Material Selection

The Radel 5010 and PKXA .517 composites were initially selected for evaluation in this task. However, the 300P system was substituted for the PKXA based upon mechanical properties data obtained during Task I. It also became apparent that a new

batch of PKXA resin would not be available in time to be included in Task II. The cladding material selected was 10-mil titanium, 6Al-4V.

### 2.2.2 Metal Clad Laminate Fabrication

Composite preparation consisted of press molding the laminates using parameters established in Task I and then secondarily bonding the titanium cladding to both laminate faces. Laminate faying surfaces were prepared for bonding by abrading with Scotchbrite pads followed by solvent wiping with ethyl alcohol. Titanium facings were prepared by chromic acid anodizing.

The titanium cladding was bonded to the Radel 5010 and 300P laminates with Radel 5010 resin and 300P resin, respectively. Several coats of resin solution, Radel 5010/DMF or 300P/DMF, were applied to faying surfaces of the laminates and titanium. The solvent was removed after each coat using the same drying cycles established in Task I for prepreg preparation. One layer of fiberglass (style 112E glass) scrim cloth was incorporated into the first or second coat of resin applied with the resin being thoroughly brushed or swept into the scrim to ensure complete wetting of the fiberglass. The titanium facings then were positioned onto the laminates and secondarily bonded using the bagging and molding cycles established in Task I.

### 2.2.3 Mechanical Properties

Mechanical properties determined on the titanium clad Radel 5010 and 300P laminates included flexural, tensile, compressive, bolt bearing, and Izod impact strength. Test methods used were the same as in Task I plus ASTM D953 and D256 for bolt bearing (Fig. 27) and Izod impact strength (Fig. 28), respectively. Tests were conducted at 75 and 250°F. Results are presented in Table IV. Test results from Task I on unclad specimens are also included in Table IV, so that the contribution of the metal cladding to the performance of the composite can be determined. As expected, the titanium cladding does increase the strength and modulus of the composite compared to unclad laminates with the largest gains being registered in flexural strength and modulus.

The metal clad composites also were tested in tension fatigue ( $r = 0.1$ ) at 60 and 80% of ultimate load. Tests were conducted at 75 and 250°F. Results are presented in Table V and are shown graphically in Figure 29. The low cycles to failure are felt to be due to the hybrid characteristics of the specimens, which permitted a progressive-type failure to occur. It is possible that the bond between the cladding and graphite





Figure 27: BOLT BEARING TEST SPECIMENS

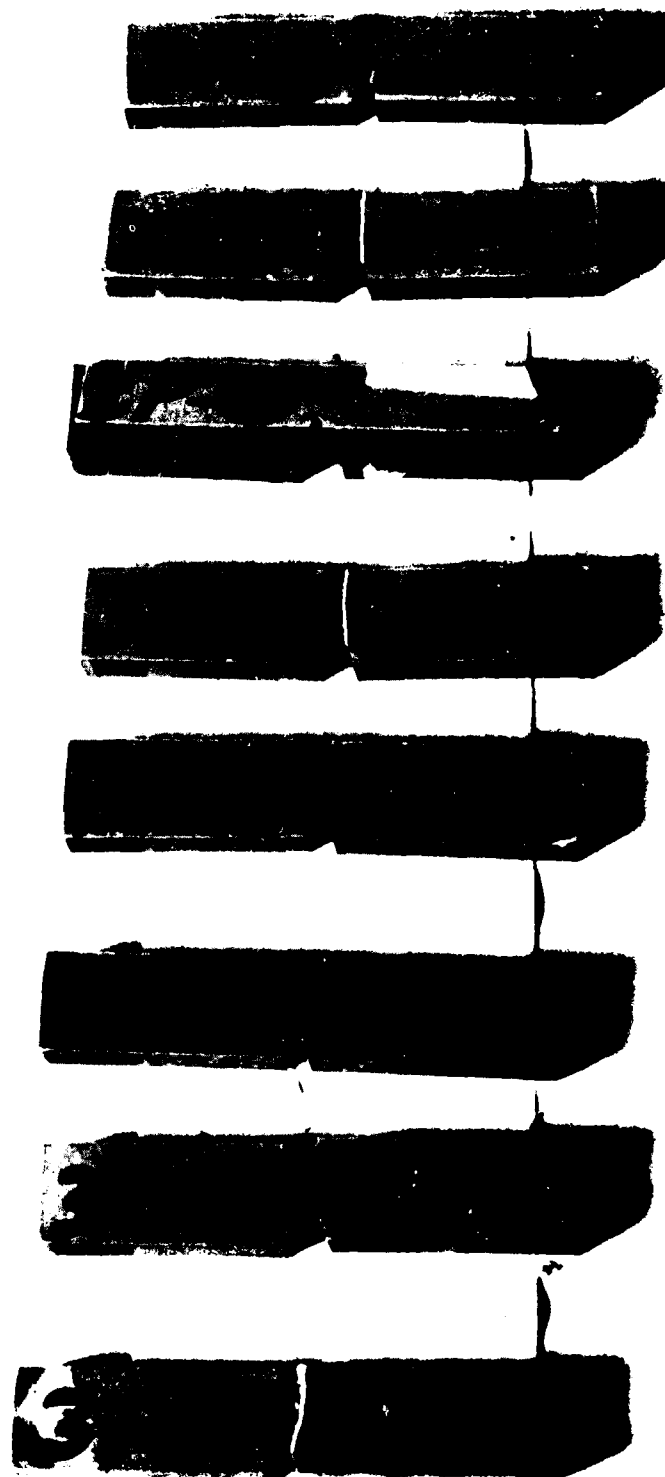


Figure 28: IZOD IMPACT STRENGTH SPECIMENS

TABLE IV—METAL CLAD COMPOSITES—MECHANICAL PROPERTIES

| Properties                                  | Radel 5010    |              |              |              | 300P |
|---|---------------|--------------|--------------|--------------|------|
|   | 75°F          | 250°F        | 75°F         | 250°F        |      |
| Test Temperature                            |               |              |              |              |      |
| Tension                                     |               |              |              |              |      |
| Strength, x 10 <sup>3</sup> psi             | 94.4 (63.0)   | 74.9 (59.0)  | 86.0 (71.0)  | 73.6 (57.0)  |      |
| Modulus, x 10 <sup>6</sup> psi              | 8.8 (8.3)     | 8.2 (7.6)    | 9.4 (8.2)    | 8.7 (7.7)    |      |
| Compression Strength, x 10 <sup>3</sup> psi | 69.4 (60.5)   | 50.1 (53.9)  | 81.2 (70.8)  | 64.2 (53.7)  |      |
| Bolt Bearing, x 10 <sup>3</sup> psi         | 55.6          | 45.3         | 65.8         | 55.0         |      |
| Impact Strength, ft-lb/in.                  | 9.3           | --           | 12.6         | --           |      |
| Flexure                                     |               |              |              |              |      |
| Strength, x 10 <sup>3</sup> psi             | 151.1 (102.3) | 136.0 (84.9) | 175.3 (89.0) | 136.5 (56.3) |      |
| Modulus, x 10 <sup>6</sup> psi              | 11.7 (8.1)    | 11.6 (7.7)   | 13.0 (8.6)   | 12.8 (5.9)   |      |

NOTES:

1. Five specimens per condition.
2. Values in ( ) are for unclad specimens from Table II.

TABLE V—TENSION FATIGUE, METAL CLAD COMPOSITES

| Material   | Cycles to Failure | Static Test Ultimate Load (lb) | Stress Ratio | Fatigue Test Maximum Load (lb) | Test Temp. (°F) |
|------------|-------------------|--------------------------------|--------------|--------------------------------|-----------------|
| Radel 5010 | Static            | 4,100                          | Static       | Static                         | 75              |
| Radel 5010 | Static            | 3,640                          | Static       | Static                         | 250             |
| 300P       | Static            | 5,800                          | Static       | Static                         | 75              |
| 300P       | Static            | 5,420                          | Static       | Static                         | 250             |
| Radel 5010 | 12,000            | Fatigue                        | 0.1          | 80% 3,200                      | 75              |
| Radel 5010 | 40,000            | Fatigue                        | 0.1          | 60% 2,460                      | 75              |
| Radel 5010 | 1,000             | Fatigue                        | 0.1          | 80% 2,912                      | 250             |
| Radel 5010 | 48,000            | Fatigue                        | 0.1          | 60% 2,184                      | 250             |
| 300P       | 2,000             | Fatigue                        | 0.1          | 80% 4,640                      | 75              |
| 300P       | 26,000            | Fatigue                        | 0.1          | 60% 3,480                      | 75              |
| 300P       | 10,000            | Fatigue                        | 0.1          | 80% 4,336                      | 250             |
| 300P       | 35,000            | Fatigue                        | 0.1          | 60% 3,252                      | 250             |

NOTE: Fatigue test rate: 1800 cpm.

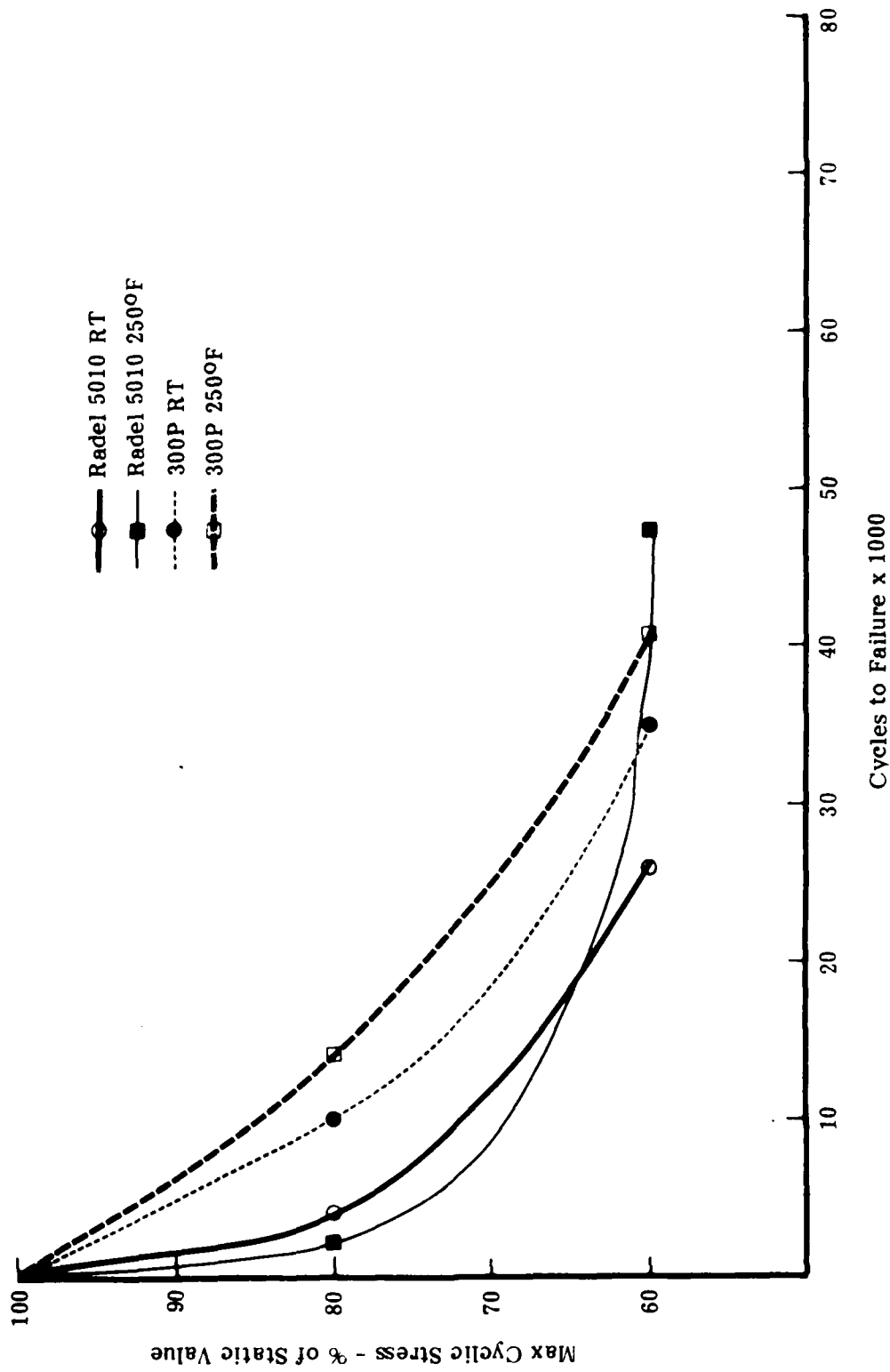


Figure 29. Constant-Amplitude Fatigue Properties of Titanium Clad Composites

composite core failed first in localized areas, then the cladding and finally the graphite composite failed. Since the ultimate strength of the metal clad composite was found to be significantly greater than for unclad composites (Table IV), once the metal cladding has failed in these tests, the graphite composite "core" must certainly fail shortly thereafter. It is appropriate to point out that the primary purpose of the metal cladding in this program was to afford fluid protection to the graphite composite core rather than increase fatigue life per se.

#### 2.2.4 Environmental Exposure

To determine whether metal cladding imparted improved fluid resistance to graphite fabric/Radel 5010 and 300P laminates, stressed and unstressed flexure specimens were immersed in two of the fluids used in Task I and the results compared to those obtained in Task I using unclad specimens. The fluids were MIL-L-7808 synthetic lubricant and MIL-H-83306 hydraulic fluid. All exposures were performed at 75°F. The stressed flexural specimens were prestressed to 60% of the control values, as the specimens evaluated in Task I had been. The results were disappointing: all Task II stressed and unstressed metal clad specimens failed within 7 to 14 days; i.e., the metal clad specimens were less resistant to fluid attack than the unclad specimens.

Examination of the failed specimens revealed that the failure mode was delamination within the graphite composite near either one (Fig. 30) or both (Fig. 31) metal clad facings. In all cases, the adhesive joint between the titanium cladding and graphite composite remained intact, with the delamination occurring interlaminarly between the graphite/Radel 5010 or graphite/300P plies, depending upon which laminate was being tested. The manner in which the titanium cladding and adjacent graphite ply(s) peeled away from the remainder of the specimen (Fig. 30 and 31) indicates that residual thermal stress from bonding the cladding to the graphite composite was the most probable cause of the earlier than expected failures. The cladding was secondarily bonded to the graphite-reinforced composite at high temperatures: 745°F for Radel 5010 and 640°F for 300P laminates. At these high bonding temperatures, the titanium cladding with a coefficient of thermal expansion ( $\alpha$ ) of  $5 \times 10^{-6}$  in./in./°F had expanded considerably more than the graphite composite with a  $\alpha$  near zero. Subsequently, at room temperature, the titanium cladding, trying to return, i.e., shorten, to its original length, would tend to peel away from the graphite composite as, in fact, it did (Fig. 30 and 31). Since the nonclad Radel 5010 and 300P unstressed specimens were not affected (Task I) by immersion in the same fluids as used in this

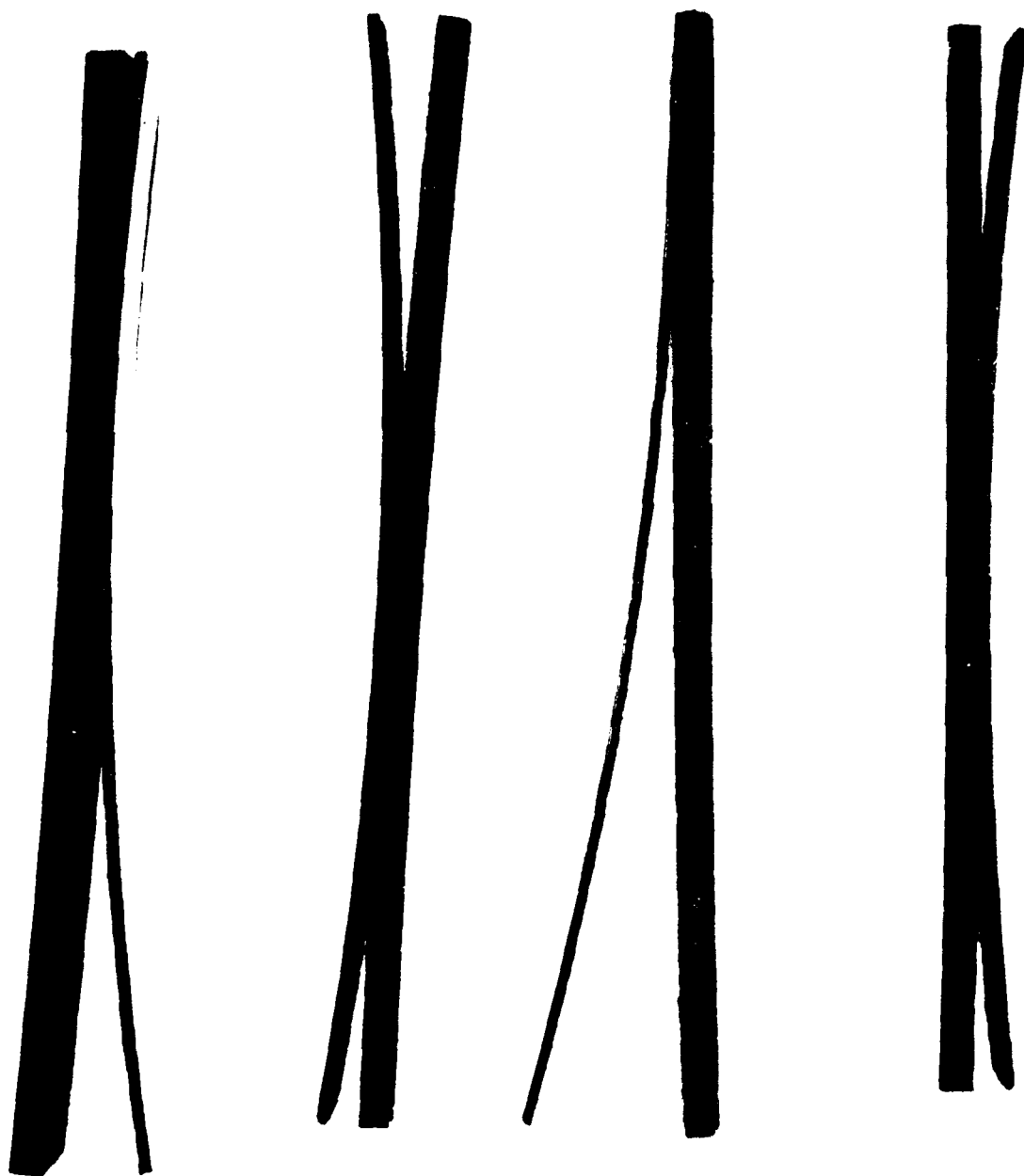


Figure 30: ENVIRONMENTAL EXPOSURE SPECIMENS - DELAMINATION ONE SIDE



Figure 31: ENVIRONMENTAL EXPOSURE SPECIMENS - DELAMINATION BOTH SIDES



task, it is apparent that the residual stress from bonding the titanium cladding degraded the fluid resistance of the composites considerably. The problem could be circumvented by using a low cure temperature adhesive. However, since the fluid attack occurred at the exposed specimen edge, as it did in previous work (ref. 3), it appears that cladding should not be relied upon for protection from fluids unless the cladding is applied to all surfaces.

#### 2.2.5 Forming Studies

The ability to postform the titanium metal clad Radel 5010 and 300P composites was demonstrated on the forming tool shown in Figure 32. The forming tool consists of a steel base plate onto which various diameter rods were welded. The laminates then are postformed over these rods.

Metal clad laminates were fabricated as described in Section 2.2.2, cut to size, positioned on the forming tool as shown in Figure 32, vacuum bagged, and formed in an autoclave at 200 psi. Forming temperatures for the Radel 5010 and 300P were 745 and 650°F, respectively. The 0.125-inch-thick specimens were successfully postformed in this manner (Fig. 33) to a minimum radius of 0.062 inch. The titanium cladding apparently did not detract from the postforming capabilities of the graphite-reinforced thermoplastic composites.

#### 2.2.6 Thermal Cycling

A prevalent concern when adhesively bonding materials that have different thermal coefficients of expansion is that the residual thermal stress induced during the bonding cycle will cause disbonding during subsequent thermal cycling. This would be especially pertinent in the case of the metal clad composites studied during this program because of the extremely high bonding temperatures used: 745°F for Radel 5010 and 640°F for 300P. To determine the effect of thermal cycling on the metal clad composites, specimens that had been postformed (Sec. 2.2.5) were cycled 50 times from -65 to 250°F. No disbonding occurred. Also, the thermal cycling caused no apparent dimensional change in the specimens.

### 2.3 TASK III—REPAIR EVALUATION

Aircraft manufacturers and users generally concede that composite structures such as graphite-reinforced epoxies are more difficult to repair than metallic structures. This subject, maintenance/repair of composites, was the topic of a Navy-sponsored work-

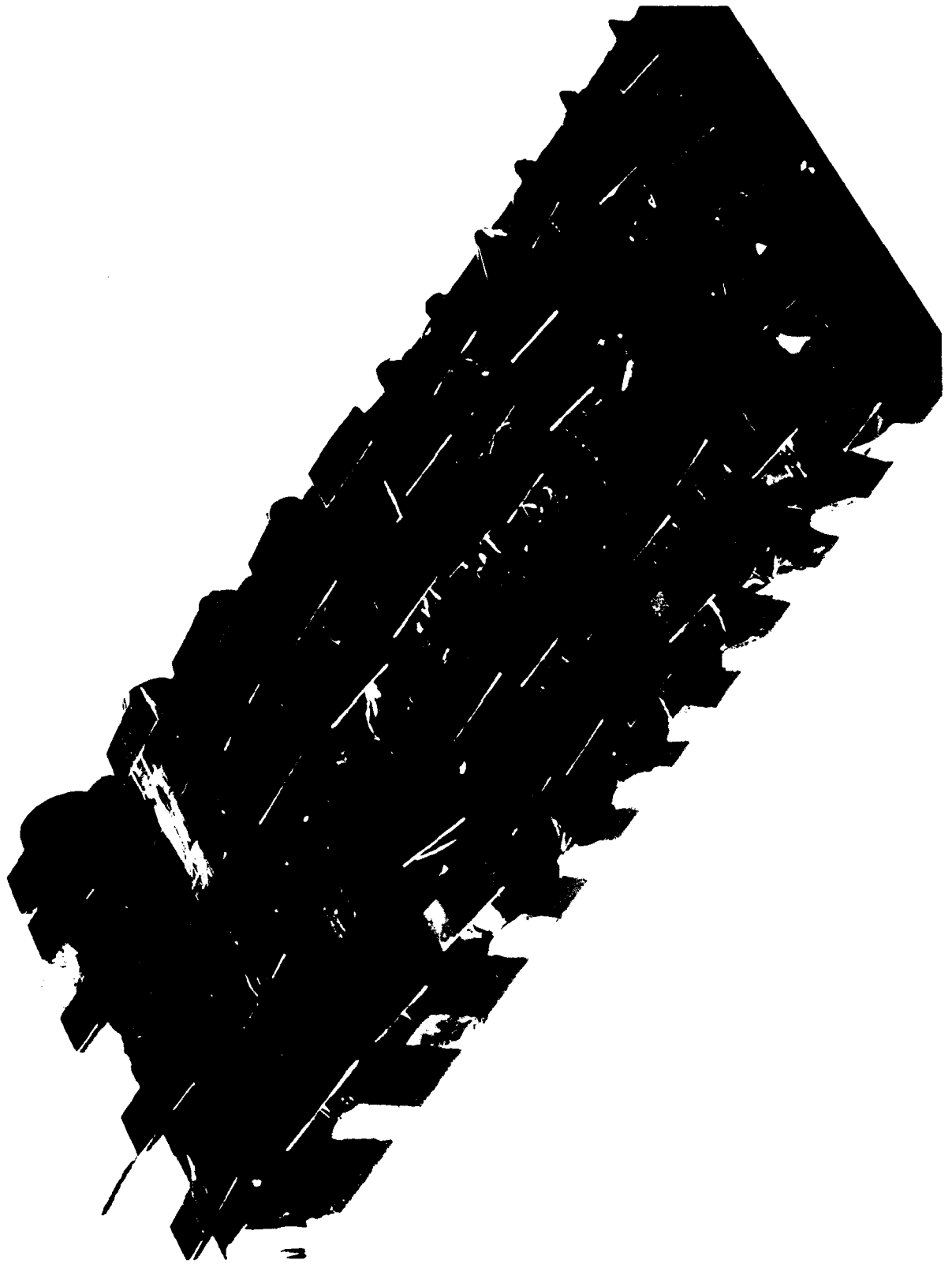


Figure 32: POSTFORMING METAL CLAD COMPOSITES



Figure 33: POSTFORMED METAL CLAD COMPOSITES

shop (ref. 6) at which fast, reliable, and easy to perform structural repair procedures for composites were cited as being critically needed. The fast processing cycles and unlimited storage life at room temperature of thermoplastics make them better suited to achieve the desired quick, reliable repairs than the epoxy materials presently used. Some complementary efforts have been performed in this area. For example, the adequacy of repairing graphite-reinforced thermoplastic composites with thermoplastic materials was successfully demonstrated under the reference 4 program using a vacuum bag and heat gun to simulate field repair of holes up to 3 inches in diameter. Also, the reference 4 and 7 programs showed that structural bond joints can be achieved using thermoplastic adhesives. In particular, a NASC program (ref. 7) demonstrated good bond strengths with the Radel 5010 resin.

Since most repairs require that a repair patch be attached to the part being repaired, two procedures for accomplishing this operation quickly with readily available equipment were evaluated during this part of the program. The procedures studied were spot fusion, which is analogous to spot welding of metals, and the use of a glue gun. The adherends used to represent the structure being repaired were T300/934 graphite/epoxy unidirectional laminates (0.045 inch thick). Two materials were used as repair patches: T300/934 unidirectional laminates and graphite fabric/P1700 polysulfone laminates (0.055 inch thick). Surface preparation consisted of hand sanding followed by wiping with clean cloths moistened with ethyl alcohol.

#### 2.3.1 Spot Fusion Repair Procedure

The spot fusion procedure consisted of abrading and solvent wiping the faying surfaces as mentioned above, assembling the lap joint as shown in Figure 34, and applying heat for 6 minutes to each spot with a soldering iron. The maximum temperature attained at the lap joint faying surfaces was 525°F. As shown in Figure 34, heat from the soldering iron was conducted into the laminate through a 0.050-inch piece of titanium. The titanium plugs and Transite sheets (Fig. 34) were held in intimate contact with the lap joint adherends with "C" clamps.

After fusion, the apparatus was disassembled and the lap joints were cut into individual specimens containing one fused spot per specimen. The specimens were then tested at 75°F. The previously established goal of 500 lb per spot was achieved whenever 0.010-inch-thick P1700 or 0.007-inch-thick Radel 5010 unsupported film was used as an adhesive. One of the specimens, after testing, is shown in Figure 35.

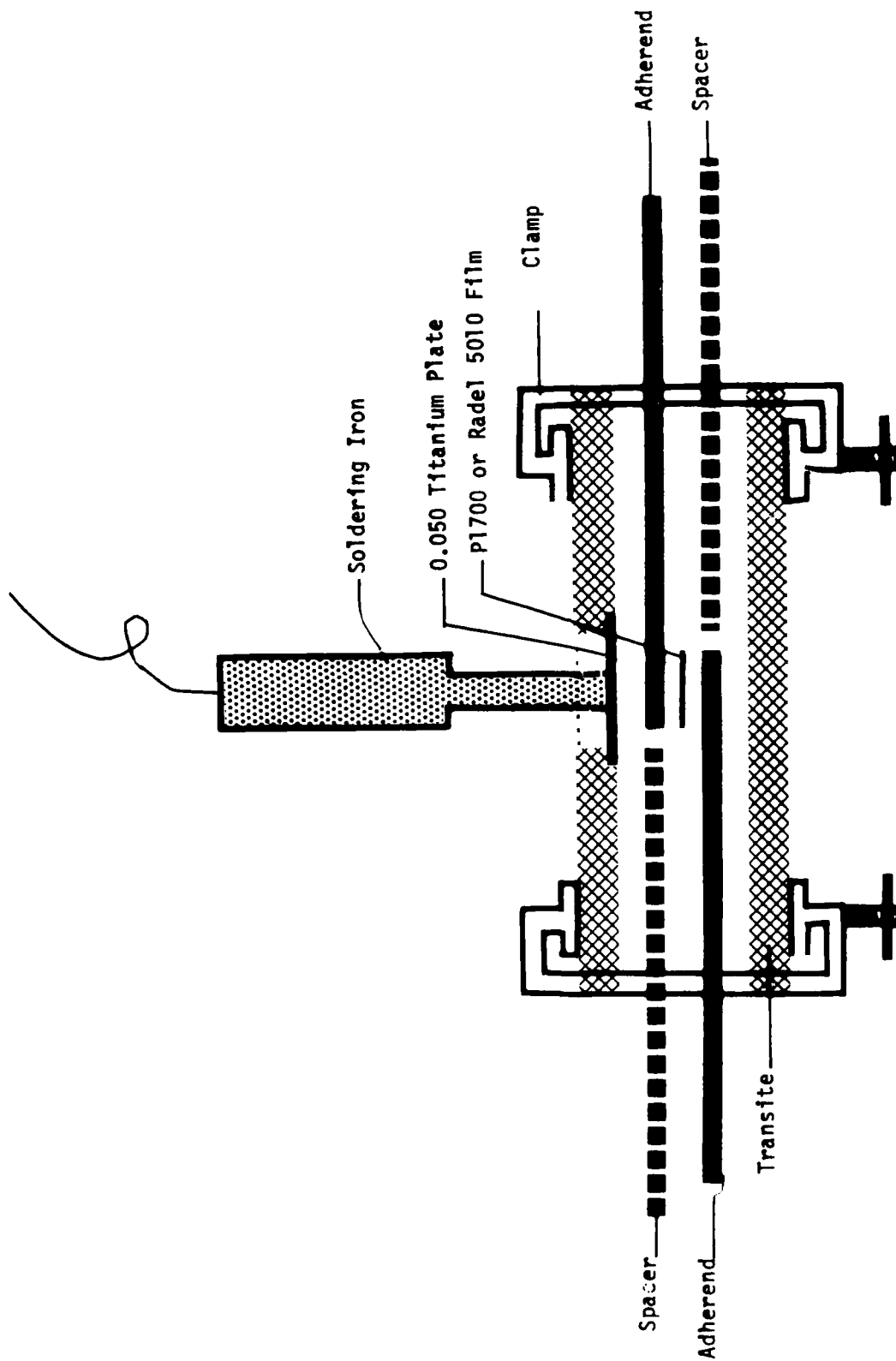


Figure 34. Spot Fusion Setup



Figure 35: SPOT FUSION TEST SPECIMEN

Visual examination of the specimens indicated that some decompaction of the P1700 adherends occurred adjacent to the spots. This decompaction could be eliminated with refinement to the fusion process.

The epoxy adherends lost their surface gloss and were probably degraded in areas contacted by the titanium plugs (Fig. 34). It is recognized that the spot fusion temperatures used are too high for the epoxy adherends and some degradation was expected. One solution to this is to use a thermoplastic film that flows at 400°F or lower.

These studies demonstrated the feasibility of spot fusion as a process for joining adherends during repair operations. Areas requiring further study include use of lower melting temperature film and optimization of the spot fusion apparatus/procedure.

#### 2.3.2 Glue Gun Repair Procedure

The use of glue guns for joining parts is firmly established for nonstructural, nonaerospace products. The desirable features of the glue gun process are low cost and fast cycle times. The primary deterrent to this process for structural repair is lack of suitable adhesive. Process development efforts are needed in this area. However, the glue gun process has the potential of being easier to perform than currently used techniques for repairing metallic construction.

A glue gun with the 600-700°F temperature capability required of polysulfone, PKXA, or Radel 5010 resins could not be acquired, so the suitability of the glue gun process was demonstrated using an available 350°F glue gun and resorcinol resin. It is recognized that the resin does not possess the environmental resistance required for structural joints. The graphite/epoxy laminate representing the structure to be repaired was prepared by abrading and solvent wiping as was the 0.026-inch-thick graphite fabric/P1700 laminate representing the repair patch. The resin was extruded onto the graphite/epoxy laminate. Then, the graphite/P1700 laminate was quickly positioned to form a lap joint and held in place for 5 to 10 seconds using finger pressure. Joints made in this manner were sufficiently strong to fail the 0.026-inch-thick P1700 laminate in tension during lap shear testing. After demonstrating this process on 1-inch-wide adherends, the process was repeated using adherend up to 12 inches wide. The purpose of using the wider adherend was to determine if suitable flow and surface wet-out could be achieved on larger areas, which would be the case

in most repair applications. The bond joints were disassembled and visual inspection showed good resin flow and surface wetting.

Based upon these preliminary evaluations, use of a glue gun appears feasible for making quick, easy-to-perform repairs. For thin-gage materials, this technique is especially attractive since the need for special equipment for applying bonding pressure is eliminated. Further efforts are needed in all areas from resin and equipment selection or development to large-area repair verification.



### 3.0 CONCLUSIONS AND RECOMMENDATIONS

The major areas studied in this program included: (1) determining if thermoplastic resins with better environmental resistance than P1700 were available, (2) evaluating metal clad composites, and (3) demonstrating easy-to-perform repair procedures using thermoplastic materials. The conclusions reached from these studies and recommendations for further study are presented in this section.

#### 3.1 CONCLUSIONS

##### 3.1.1 Task I—Resin and Composite Characterization

Impregnation and laminate processing parameters were established for graphite fabric/Radel 5010, PKXA .41 and .517, 300P, KM-1, and CM-1 systems. All of these systems were superior to P1700 in resistance to methylene chloride, which is the solvent predominantly used in removal of organic aircraft finishes. Exposure of flexure specimens in JP-4 fuel, MIL-H-5606 hydraulic fluid, MIL-L-7808 synthetic lubricant, MIL-H-83306 hydraulic fluid, and salt water in both the stressed (60% of ultimate) and unstressed modes for 28 days on graphite fabric/Radel 5010 and graphite fabric/300P systems showed: (1) the unstressed specimens were not appreciably affected by the fluids, with the greatest reduction (30%) in strength occurring on the Radel 5010 specimens immersed in MIL-H-83306 hydraulic fluid; (2) stressed graphite/Radel 5010 specimens were not significantly affected except for the MIL-H-83306 exposure, which delaminated the specimens; and (3) stressed graphite/300P specimens delaminated in all of the fluids.

Graphite fabric/KM-1 and CM-1 flexure specimens were cut into small samples and immersed in the same fluids as the Radel 5010 and 300P laminates plus one additional fluid: methylene chloride. Visual examination of the samples showed no detectable effects for periods to 30 days except for the KM-1 specimens in methylene chloride, which started degrading after 2 days immersion.

Mechanical properties of Radel 5010 and 300P laminates were equivalent to polysulfone laminates. The PKXA .41 and .517 laminates exhibited lower mechanical properties than the other systems, but these results could be attributed to overaging of the resins prior to impregnation.

The graphite fabric/KM-1 and CM-1 systems exhibited potential of possessing mechanical properties comparable to polysulfone laminates as measured by flexure and short beam shear tests. However, significant scatter in test results was obtained, indicating a variability in either the materials or processes used.

### 3.1.2 Task II—Metal Clad Composites

Graphite fabric/PKXA and 300P laminates were prepared using procedures established in Task I. The laminates were then clad by secondarily bonding 0.010-inch titanium 6Al-4V to each face.

Mechanical properties determined were tension, compression, flexure, bolt bearing, and impact strength. The titanium-clad specimens showed improved mechanical properties compared to results obtained in Task I on unclad specimens.

Resistance of the clad laminates to MIL-L-7808 synthetic lubricant and MIL-H-83306 hydraulic fluid exposure was less than for unclad laminates tested in Task I. The stressed and unstressed metal-clad flexure specimens failed in 7 to 14 days after immersion in the exposure fluids. These earlier than expected failures were postulated to be due to residual thermal stresses set up by the elevated temperature bonding process used to join the titanium cladding to the laminates. Since the fluid attack occurred at specimen edges, it is concluded that metal cladding should not be relied upon for preventing composite degradation due to fluid exposure.

Thermal cycling from -65 to 250°F had no deleterious effect on titanium-clad graphite fabric/Radel 5010 and 300P laminates.

Titanium-clad graphite fabric/Radel 5010 and 300P laminates can be postformed at 745°F and 650°F, respectively, using 200 psi forming pressure.

### 3.1.3 Task III—Repair Evaluation

Spot fusion and use of a glue gun are feasible methods for joining graphite/epoxy and graphite/thermoplastic repair patches to graphite/epoxy structure.

### 3.2 RECOMMENDATIONS

Based upon the results of this program, the CM-1 and KM-1 resins are more resistant to fluids than P1700 polysulfone and, possibly, epoxies. The processing of these laminates should be optimized and their fluid resistance thoroughly evaluated.

A new batch of PKXA resin should be evaluated for storage stability. The effect of laminating parameters on fluid resistance and postforming capabilities should be determined.

When comparing results of this program with previous efforts (ref. 3), there is reason to suspect that graphite fabric reinforced composites are less resistant to fluid attack than laminates with unidirectional graphite tape reinforcement. This aspect should be evaluated.

In the area of repairs, it is recommended that the fusion and glue gun repair processes be developed for use at repair facilities and aboard ship. Both material and equipment development/evaluation are required. The goal of these efforts should be the development of a repair procedure that is more reliable and easier to perform than processes used for repairing metallic construction.

## REFERENCES

1. Hoggatt, J. T., "Study of Graphite Fiber Reinforced Thermoplastic Composites," D180-18034-1, Boeing Aerospace Company, Seattle, Washington, February 1974.
2. Hoggatt, J. T. and Von Volkli, A. D., "Evaluation of Reinforced Thermoplastic Composites and Adhesives," D180-17503-3, Boeing Aerospace Company, Seattle, Washington, Seattle, Washington, March 1975.
3. Hoggatt, J. T. and Hill, S. G., "Development of Hybrid Thermoplastic Composites," D180-18752-3, Boeing Aerospace Company, March 1977.
4. Contract F33615-76-C-3048, "Advanced Fiber Reinforced Thermoplastic Program."
5. Unpublished data, Boeing Aerospace Company, Seattle, Washington.
6. Proceedings from the NASC Composite Materials Maintenance/Repair Workshop, September 26-28, 1978, San Diego, California.
7. Hoggatt, J. T., Hill, S. G., and House, E. E., "Environmental Exposure on Thermoplastic Adhesives," D180-24744-1, Boeing Aerospace Company, Seattle, Washington, December 1978.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

| REPORT DOCUMENTATION PAGE   |                       | READ INSTRUCTIONS<br>BEFORE COMPLETING FORM                               |
|---|-----------------------|---|
| 1. REPORT NUMBER<br>14) D180-25734-1  | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER   |
| 4. TITLE (and Subtitle)<br>Advanced Thermoplastic Composite Development   |                       | 5. TYPE OF REPORT & PERIOD COVERED<br>9) Final Report 4 Nov 77 - 4 Feb 79 |
| 7. AUTHOR(s)<br>10) S. G. Hill, E. E. House, J. T. Hoggatt  |                       | 6. PERFORMING ORG. REPORT NUMBER  |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Boeing Aerospace Company<br>P. O. Box 3999<br>Seattle, Washington 98124  |                       | 8. CONTRACT OR GRANT NUMBER(s)<br>13) N00019-77-C-0561                    |
| 11. CONTROLLING OFFICE NAME AND ADDRESS<br>Naval Air Systems Command (AIR 5163D3)<br>U. S. Department of the Navy<br>Washington, D.C. 20360   |                       | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS<br>14) 1      |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)<br>11) May 79   |                       | 12. REPORT DATE   |
|   |                       | 13. NUMBER OF PAGES   |
|   |                       | 15. SECURITY CLASS. (of this report)<br>Unclassified                      |
|   |                       | 15a. DECLASSIFICATION DOWNGRADING SCHEDULE                                |
| 16. DISTRIBUTION STATEMENT (of this Report)<br>Approved for public release: Distribution Unlimited  |                       |   |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  |                       |   |
| 18. SUPPLEMENTARY NOTES   |                       |   |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number)<br>Polysulfone Radel 5010<br>Polyphenylsulfone P-300<br>Polyethersulfone KM-1<br>Thermoplastic polymers CM-1<br>PKXA Graphite/Thermoplastic Composites   |                       |   |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>The objective of this program was to evaluate recently developed thermoplastic resins as matrix materials for graphite reinforced composites.<br>Thermoplastic polymers (PKXA Polysulfone, Radel 5010 polyphenylsulfone, P-300, and KM-1 polyethersulfones, and CM-1 fluorocarbon based resin) having high temperature capability (+350°F) were evaluated as matrix materials for graphite reinforced composites. Resin characterization studies were performed. Prepreg processing and laminate molding parameters were optimized. Mechanical → |                       |   |

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## #20 Abstract Continued

properties evaluations conducted consisted of flexure, tension, compression, shear, bearing, and impact strength. A study was conducted to determine resistance of the graphite fabric/thermoplastic composites to fluids likely to be encountered in aircraft flight and maintenance operations.

Thin (0.010") titanium sheet was bonded to the laminate faces and these "clad" specimens immersed in fluids to determine if the clad specimens were more fluid resistant than unclad specimens. Postforming and thermal cycling studies were performed on the clad specimens.

The feasibility of using two joining methods, spot fusion and use of a glue gun, for attaching graphite reinforced composite repairs patches to graphite reinforced composite structure was demonstrated.

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